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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 2

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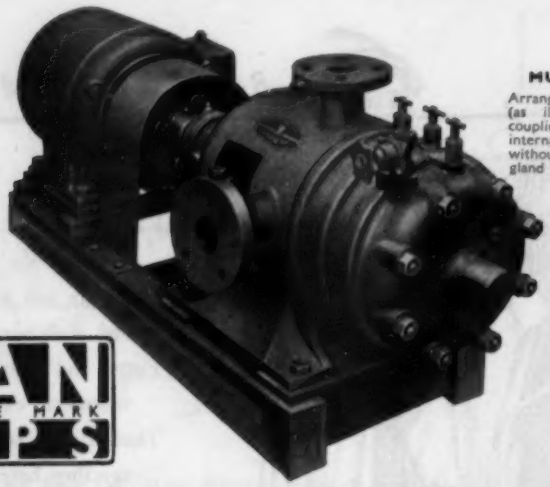

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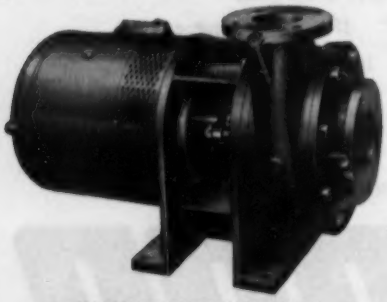

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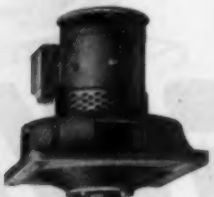

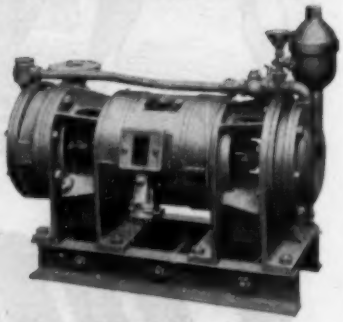

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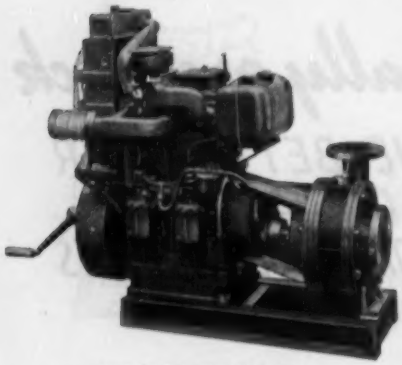

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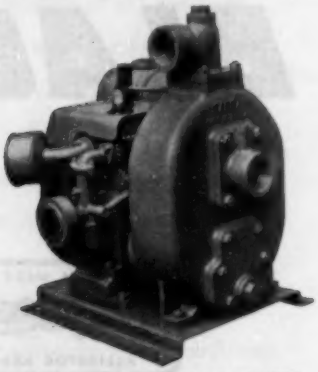

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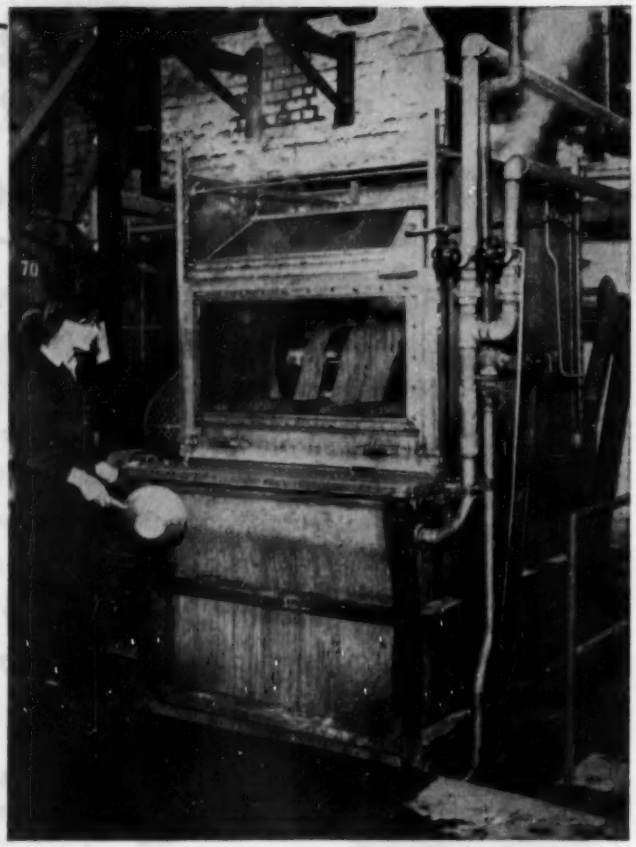

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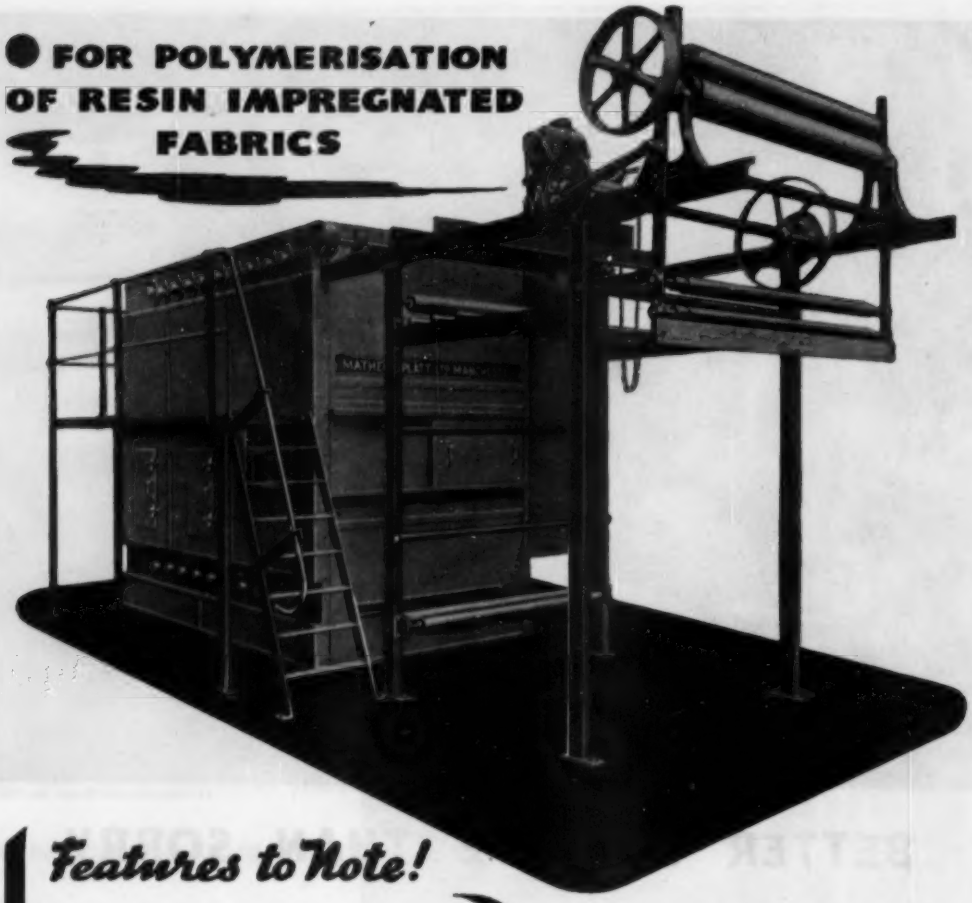

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 229–232 of the July 1953 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Pressure Dyeing and Bleaching with special reference to Recent Developments *F. H. Marsh*

COMMUNICATIONS

The Design and Construction of a Differential Refractometer for Measurements on Coloured Solutions *E. Atherton and E. Cowgill*

The Polarography of Azo Dyes *J. de O. Cabral and H. A. Turner*

The Formation of Polymers in Wool *G. W. Madaras and J. B. Speakman*

The Combination of Wool with Acids *L. Peters and J. B. Speakman*

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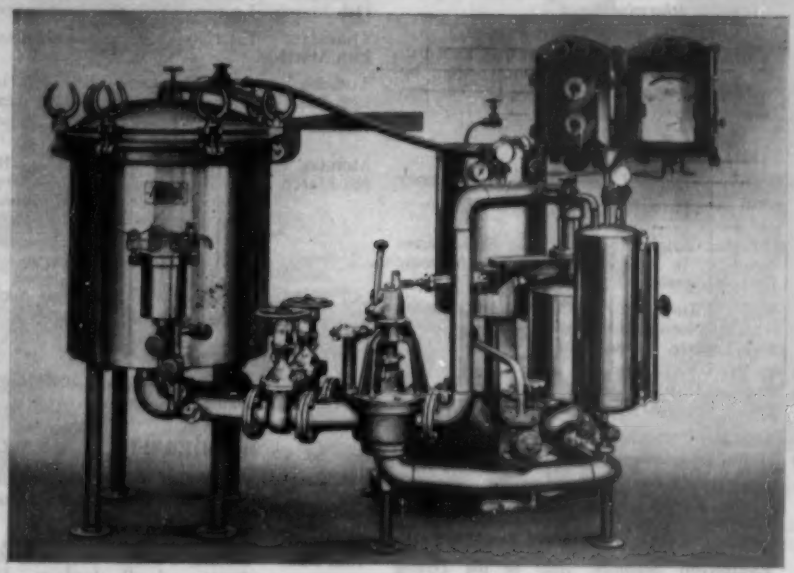

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FORTHCOMING MEETINGS OF THE SOCIETY

Thursday—8th April 1954 at 7-30 p.m.

ELEVENTH MERCER LECTURE N. W. Yelland, A.R.C.S., B.Sc., D.I.C. *Physics in the Dyeing, Printing, and Finishing Industries* Midland Hotel, Manchester 2

Friday—30th April 1954

ANNUAL GENERAL MEETING and DINNER of the Society Midland Hotel, Manchester 2

SCOTTISH SECTION

All Meetings in St. Enoch Hotel, Glasgow, at 7.0 p.m., unless otherwise stated

1954	
Tuesday 23rd March	ANNUAL GENERAL MEETING OF THE SECTION. To be followed by three short papers by Sectional members — details to be announced later

MIDLANDS SECTION

Except when stated otherwise, Lecture Meetings commence at 7.0 p.m.

1954	
Wednesday 24th Feb.	Douglas Haigh, Esq., A.T.I. *Some recent researches in the Dyeing of Felt.* Masonic Hall, Nuneaton
Thursday 4th March	R. F. Wilson, Esq. (B.C.C.) (Joint meeting with the Nottingham Textile Society). *Colour.* Gas Theatre, Nottingham
Wednesday 17th March	G. H. Lister, Esq., B.Sc., Ph.D. *The Migration Properties of Acid and Chrome Dyes.* Victoria Station Hotel, Nottingham
Friday 26th March	MIDLANDS SECTION DINNER. King's Head Hotel, Loughborough
Wednesday 7th April	ANNUAL GENERAL MEETING OF SECTION. J. A. Potter, Esq., M.A. *Dyeing and Finishing Synthetic Fibres in the Hosiery Industry.* King's Head Hotel, Loughborough
Friday and Saturday 28th - 29th May	Exhibition *Scientific Aids to the Dyeing Industry.* College of Technology, Leicester (*Details later*)

MANCHESTER SECTION

Unless otherwise stated, meetings take place at the Textile Institute, 10 Blackfriars Street, Manchester 3, and commence at 6.30 p.m.

1954	
Friday 19th Feb.	Morse Brown, Esq. *The History of Fashion*
Friday 19th March	Symposium on *Continuous Dyeing.* Five papers will be presented and details will follow. College of Technology, afternoon and evening sessions
Friday 2nd April	ANNUAL GENERAL MEETING AND ADDRESS by the Chairman, G. S. J. White, Esq.

MANCHESTER JUNIOR BRANCH

All lectures to be held in the Reynold's Hall, Manchester College of Technology, at 6.30 p.m.

1954	
Monday 8th March	D. G. Evans, Esq., B.Sc. *Cibalan Dyes — Nylons and Nylon Unions*

WEST RIDING SECTION

Meetings held at the Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated

1954	
Thursday 25th Feb.	A. R. Smith, Esq., B.A., B.Sc., A.R.I.C. (British Industrial Plastics Ltd.). *The Application of Resins to Textiles*

WEST RIDING SECTION (*continued*)

Thursday 11th March	Prof. J. B. Speakman (The University, Leeds). Lecture. Title to be announced later
Thursday 25th March	LECTURE AND ANNUAL GENERAL MEETING
Tuesday 12th Jan.	S. Kershaw, Esq., F.T.I. (By invitation of the Yorkshire Section of the Textile Institute). *Experiences on a United Nations Assignment.* Midland Hotel, Bradford, at 7.15 p.m.
Monday 8th March	G. Kenneth Seddon, Esq. (By invitation of the Bradford Textile Society). *Interesting Points in Dyeing and Finishing.* Midland Hotel, Bradford, at 7.15 p.m.

LONDON SECTION

All Meetings will be held at the Royal Society, Burlington House, Piccadilly, London W.1, at 6.0 p.m. unless otherwise stated

1954	
Friday 5th March	*The London Lecture.* Subject, Speaker and venue to be given

HUDDERSFIELD SECTION

All Lectures at Field's Cafe, Westgate, Huddersfield, at 7.30 p.m. unless otherwise stated

1954	
Tuesday 16th Mar.	ANNUAL GENERAL MEETING, followed by a lecture, *Fastness Properties for Users Satisfaction.* J. S. Ingham, Esq. (Marks & Spencer Ltd., London)

BRADFORD JUNIOR BRANCH

All Meetings held at Bradford Technical College commencing at 7.15 p.m. unless otherwise stated

1954	
Thursday 25th Feb.	Junior Branch Dance
Friday 12th March	Students' Competition Evening

LEEDS JUNIOR BRANCH

All meetings held in the Colour Chemistry Lecture Theatre, The University, Leeds 2, on Tuesdays at 3.30 p.m.

1954	
Tuesday 9th Mar.	Dr. G. H. Lister (Messrs. Sandoz Products Ltd.). *Migration Properties of Acid and Chrome Dyes*

NORTHERN IRELAND SECTION

All Meetings to be held in Royal Avenue Hotel, Belfast, at 7.30 p.m.

1954	
Friday 5th March	J. Potter, Esq. (Clayton Aniline Co. Ltd.). *Special Finishes for Textiles and Their Evaluation.* (Joint meeting with Foremen Dyers Guild)
Late March or early April	ANNUAL GENERAL MEETING AND DINNER. (*Details later*)

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THE JOURNAL

OF THE

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Volume 70 Number 2 FEBRUARY 1954 *Issued Monthly*

Proceedings of the Society

Azoic and other Fast Dyeings on Knitted Cotton Fabric

E. R. WILTSHIRE

Meeting of the Midlands Section held in the College of Technology, Leicester, on 25th February 1953
Mr. A. P. Kershaw in the chair

Methods of dyeing the azoic dyes on knitted cotton fabrics on the winch are described. The application of the coupling component is straightforward, but development can cause difficulty. Relatively few developers can be processed satisfactorily on the winch, and as a general method pad development is recommended. For this purpose the fabric should preferably be dried after application of the coupling component. The final aftertreatment of azoic dyeings is done very efficiently on the winch.

Pale shades can be dyed with vat dyes on the winch if adequate quantities of Dispersol VL are employed. The technique described is simple and has advantages over the use of solubilised vat dyes, particularly for blues.

INTRODUCTION

The use of vat dyes and of their solubilised derivatives, the Soledons, and methods of producing dyed shades on the winch with these two classes of dyes, were described a few years ago [1]. The present paper will therefore deal mainly with the application of the azoic or Brenthol dyes to knitted cotton fabrics on the winch. Everyone is familiar with the general usefulness of the azoic dyes for the production of scarlets, reds, and maroons on cellulosic fibres. Their place in the normal ranges of fast dyeings on cotton is well known and in spite of many improvements in the range of vat dyes now available the azoics are still necessary to complete a fast colour range. Scarlets, wines, maroons, and bright reds generally of high fastness cannot be produced without the aid of these dyes, and the popularity of this type of shade for sports wear need not be emphasised to anyone concerned with knitted fabrics.

AZOIC DYES ON THE WINCH

The azoic dyeing process involves four steps, each of which will be considered in turn in relationship to the dyeing of knitted fabric. These four steps are as follows—

(1) Application of the azoic coupling components.

(2) Intermediate hydroextraction or drying.

(3) Development of the colour in a solution of a diazo compound.

(4) A boiling aftertreatment, usually called "soaping", but for which soap is nowadays by no means the best product to use.

Application of the Coupling Component

It is hoped that the subject of this paper is of some interest because the winch machine is not altogether ideal for the application of the azoic dyes and some difficulty has been experienced in applying this process on such a machine. If, however, the application of the coupling component itself were the only part of the process, then this paper would not be necessary, because this stage offers no difficulty to the experienced winch dyer. The coupling component, in fact, once it has been dissolved with the aid of a dispersing agent and caustic soda, can be applied to the fabric in exactly the same way as a direct cotton dye and like the latter it is generally absorbed evenly and slowly from the dyebath. A liquor : goods ratio of 30 : 1 is normally adopted. The dyebath is set at a temperature of 30–40°C. with a small quantity of caustic soda and dispersing agent. The concentrated Brenthol solution is then added slowly to the winch in the same way as if it were a direct cotton dye. An addition of common salt is made to increase the absorption to an adequate figure, but there is generally no need with normal cotton fabrics to raise the temperature. An increase in temperature will of course aid penetration, but it will also cause a decrease in the amount of Brenthol absorbed at equilibrium. The application of the Brenthol is complete in approx. 45 min., say 20 min. after the last addition of common salt.

A glance at a complete range of Brenthol shades will show that, for the production of any particular red or maroon shade, generally speaking several

alternative Brenthols may be used. The Brenthol to select for winch dyeing is governed by one consideration, that of substantivity. It is essential to use the Brenthol possessing the highest affinity for the fibre if satisfactory results in terms both of economy and of fastness are to be obtained; in fact, one can go even further than this and state that for winch dyeing only those shades should be selected that can be produced from the Brenthols possessing the highest possible affinity of their class, and for reds, this means that Brenthols BN and BC are by far the most satisfactory. If colour or fastness considerations do in fact rule out these Brenthols, then the only others to enter into consideration are Brenthols AN, BA, and CT. These possess a medium substantivity but are fairly satisfactory when common salt is added to the dyebath. Outside the scarlet, red, and maroon field the Brenthols do not generally come into consideration for winch dyeing, although there is no reason why Brenthol BT should not be used for brown shades. On the other hand, Brenthol AT for yellows and Brenthols GB and RB for blacks are not very satisfactory owing to their too stringent requirements during developing.

A perusal of most Brenthol dyeing recipes will reveal that an addition of formaldehyde is generally recommended to the Brenthol solution. This is because the Brentholated fabric before development is particularly sensitive to the action of the carbon dioxide in the atmosphere, and therefore prolonged exposure to the air in the wet state may be detrimental. The addition of formaldehyde to the Brenthol liquor largely overcomes this difficulty, and therefore it should always be added when recommended. It must also be emphasised at this point that, apart from the carbon dioxide in the air, the Brentholated fabric can be adversely affected by contamination with water, chlorine, or acids. Fabric dyers should pay particular attention to this point, as a white or light mark caused by such contamination is easily visible on knitted fabric after dyeing, whereas in the case of yarn dyeing it may easily escape notice. Whilst discussing the action of formaldehyde, it is interesting to note that the latest addition to the Brenthol range, viz., Brenthol BC, requires no such addition, as it is completely stable to carbon dioxide without addition of formaldehyde to the solution. In this respect it is unique among the red-producing Brenthols.

Hydroextraction

Between the Brentholation of the fabric and its development in a separate bath, it is necessary to remove as much as possible of the mechanically held Brenthol liquor, so that a minimum of loose pigment will be formed on the outside of the fibres and threads when the fabric is introduced into the developing bath. It is therefore necessary at this stage to hydroextract the fabric very thoroughly, but at the same time special care must be taken to avoid contamination. In practice it has been found that the best method of doing this is to run the wet fabric into sacks or bags which have already been dipped in the Brenthol solution. One roll per bag is usually satisfactory, and the bags can then be placed in the hydroextractor and whizzed without trouble. For the best results, however, it is also necessary to dry the fabric at this stage. This will be discussed again later when dealing with development, but the procedure during drying must again involve a maximum of care to avoid contamination with moisture, acid, or chlorine fumes and to avoid contact of the Brentholated fabrics with very hot metal surfaces. Drying arrangements may have to be worked out in some detail in each works, but generally it can be stated that the usual hot-air dryers are quite satisfactory for drying the Brentholated fabric at this stage provided sufficient care is taken.

Development

Whilst the amount of Brenthol on the fibre determines the depth of colour and is therefore a fundamental quantity that must be correctly applied before development commences, it is the development itself that is the most difficult operation to carry out successfully. This generalisation applies to all types of azoic dyeing, but it is particularly applicable in the case of knitted cotton goods dyed on the winch. The development of an azoic dyeing is not a dyeing operation but a chemical reaction. Moreover, it is a chemical reaction in which one of the products of reaction (the azoic pigment) is insoluble and is precipitated out of the system. Consequently the reaction is irreversible. This means that no levelling is possible once the reaction conditions have gone wrong and have produced an uneven result. Since the stripping of an azoic dyeing is undoubtedly to be avoided, it is essential to ensure that the development is carried out properly and that the correct conditions for this reaction are maintained.

When developing knitted fabric on the winch two types of difficulties can be distinguished, namely—

(1) Those due to incorrect setting of the conditions either in the original Brenthol bath or in the developer bath.

(2) Those due to the fact that development is being carried out on a winch— because it is a fact that even though the development conditions have been carefully prepared and controlled, so that they are quite correct from a chemical point of view, the mechanical conditions obtaining on a winch may, nevertheless, lead to uneven development.

It is with the latter type of difficulty that this paper is concerned, because the Brenthol and developing baths can be set correctly without difficulty if details given in the published literature are followed. If anyone is in doubt as to the way in which an azoic recipe for winch dyeing should be established then he should follow details appertaining to cotton yarn dyeing under the same liquor : goods ratio, i.e. about 30 : 1.

The practical procedure that gives best results with winch developing is to take the hydroextracted rolls of fabric and to open them out carefully by hand, plaiting them down in a clean waggon, so that they can be run on to the winch without twisting. Entry of the whole batch into the developing liquor must be made as quickly as possible, so that it is best to throw one end of the roll over the winch and to sew it to the other end before starting the

winch in motion. This ensures that the winch does not have to be stopped for sewing up with an undeveloped portion of the roll still out of the liquor. Furthermore, as the rolls are run on to the winch someone should stand at the other side pushing the fabric under the liquor immediately and not allowing it to float.

The primary object of these activities will be plain: to allow the developing liquor to do its work quickly and if possible evenly. Speed of development is in fact the main essential, for the reasons given below.

Azoic Development

The active compound absorbed on to the fabric when it is treated in the Brenthol bath is not the Brenthol itself but its sodium salt. This is the compound which actually couples up with the diazo compound to form the pigment on the fibre. The Brenthol itself is almost inactive in this respect. The instability of the sodium salt of the Brenthol has already been noted, and the ease with which it is hydrolysed back to the free Brenthol by water or weak acid necessitates the precautions already described to protect the fabric during the intermediate stages between Brentholation and development. The diazo compound, on the other hand, is also a very reactive body, but in this case, whereas it is stable in acid solutions, it is easily decomposed or converted to a non-coupling form by alkalis. It is evident, therefore, that at the point where these two compounds react conditions should preferably be neutral, i.e. neither acid nor alkaline, therefore when entering a strongly alkaline fabric into the acid developing bath the alkalinity must be neutralised to avoid decomposition of the diazo compound in the bath. On the other hand, the developing bath itself cannot be kept in a strongly acid condition, as the speed of the reaction is slowed down by an increase in the acidity, and as will be seen speed of coupling is essential for good results. Consequently the alkali is neutralised by the addition to the developing bath of a weak acid such as acetic acid or an acid salt such as aluminium sulphate as alkali-binding agent. Even so, the bath must still be kept slightly acid at the end of the reaction, since diazo compound is present in excess. Consequently on entering the Brentholated fabric into the developing bath any portion of it which has exhausted the diazo compound in the immediate neighbourhood or which is slow to couple may have the Brenthol sodium salt therein exposed to the action of a weak acid. This will result in hydrolysis of the sodium salt back to the free Brenthol, with the result that proper coupling will not take place and such portions will appear finally lighter than the rest. It is clear that this danger will be more apparent the slower the speed of coupling, and therefore every effort should be made to increase the speed to a maximum.

The speed of the chemical reaction could, of course, be increased by raising the temperature. This, however, is not permissible owing to the instability of the diazo compound, which rapidly decomposes at temperatures much above 20°c. Similarly an increase in the pH cannot be allowed or else the diazo compound again will decompose. Since therefore, the speed of the reaction between any two components cannot easily be increased, everything must be done to ensure that coupling takes place readily over the bulk of the fabric. For this purpose an adequate concentration of diazo compound must be used and in practice considerably more is required than would be calculated on an equivalent weight basis from the chemical equation. Also, as already described, every mechanical aid to adequate penetration of the developing liquor through the fabric should be made. There are, of course, limits to the steps that can be taken in this direction. Given the fact that developing on the winch is being used, these limits are severe, and it has been found in practice that only a relatively small number of azoic combinations couple readily enough to give a good result under winch conditions of application. Speeds of coupling vary from one combination to another, and it is only the fastest couplers that can be used satisfactorily on the winch. Generally speaking, with any particular Brenthol the speed of coupling is governed by the nature of the diazo compound. The fastest couplers are certain of the scarlet developers such as Brentamine Fast Scarlet GG and Brentamine Fast Scarlet R. On the other hand, blue developers are extremely slow and are quite unsuitable for winch development. In between, the others range in speed between the scarlets and the blues, but few of these intermediate ones are in fact entirely suitable when used on the winch. These intermediate developers include the important ones necessary for the production of maroons and wines such as, for instance, Brentamine Fast Bordeaux GP and Brentamine Fast Red B.

In considering the mechanical factors which influence the speed of development of the batch as a whole mention should be made of the fabric itself. A heavy, loosely knitted fabric that will sink and absorb liquor readily will be found to develop much better than a light, tightly knitted fabric which floats and is difficult to penetrate. Such factors influence the dividing line that can be drawn between those combinations suitable for winch development and those that are not, but without giving any hard and fast rules it can be stated that only the three scarlet developers—Brentamine Fast Scarlet GG, Brentamine Fast Scarlet R, and Brentamine Fast Scarlet G—have consistently given satisfactory results when developed on the winch.

We turn therefore to other methods of developing knitted fabric. It will no doubt have been noted that the requirements of immediate coupling which have already been described, namely the rapid and even penetration of a concentrated developing liquor throughout the mass of the goods, are typical of a padding operation rather than a dyeing one. Padding methods of development have in fact proved the best for azoic dyeing both on piece goods and on yarn when the manipulative difficulties have been overcome. The same has also proved true for knitted fabrics.

Padding

Padding is an operation in which a liquor is applied mechanically to a textile material.

Conventional padding mangles for piece goods, consisting of an impregnating trough and squeezing rollers, immediately spring to mind when padding is mentioned. Padding in its widest sense, however, is not necessarily restricted to piece goods in open width, as even yarn in hank form can be padded if a suitable apparatus is available. The essential requirements for padding are—

(*a*) Rapid mechanical impregnation

(*b*) An even and efficient squeeze-off or hydroextraction.

In some respects the requirements for padding are the exact opposite of dyeing, especially when the liquor being used contains a product possessing affinity for the material being padded. Such affinity can lead to an unequal distribution of the product in question from one end of the fabric to the other owing to absorption by affinity during the passage of the fabric through the padding trough. The lowest possible affinity is therefore aimed at when padding. However, when padding with a diazo compound this particular difficulty does not arise, since it has no affinity for the cellulose.

In most cases the object of padding is to furnish the fabric with an evenly distributed concentration of a particular product or products, and considerable experience of the design of machines and the control of working conditions is necessary to attain this end. In the case of the development of an azoic dyeing, however, the Brenthol already on the fibre fixes the depth and the levelness, and the developing operation consists merely in presenting this Brenthol with an excess of diazo compound, so that satisfactory coupling can take place. The conditions for padding when developing are therefore not critical, although a large excess of developer may result in some dulling of the shade if not washed off immediately.

The point being emphasised, of course, is that pad development is not a difficult operation and that because of the wide latitude allowable with regard both to the quality of the nip or expression and the concentration of liquor applied to the fabric, the successful development of a Brentholated knitted cotton fabric on the pad is in fact a feasible proposition.

Padding mangles are not unknown items of equipment even in knitted-fabric dyehouses. In the latter case they are usually of very light construction and are made so that the circular fabric can run over the usual steel stretcher just before entering the nip of the rollers. It is not intended to describe every practical detail of the padding operation here, but the following points of interest should be noted—

(1) The padding trough should be small, say a maximum of 5 gal. Excessively long runs to one shade are not generally likely to be required, and as the concentration of the developing solution is high, it is economically undesirable but not technically detrimental to use a large trough.

(2) A wetting agent stable to acid is desirable in the padding liquor in addition to Azopol A, which should be used in the interest of good rubbing fastness. Lissapol N is suitable for this purpose.

(3) The Brentholated fabric can be developed wet on the pad after thorough hydroextraction and opening out; but there is no doubt that, for the best levelness, penetration, and fastness to rubbing, the Brentholated fabric should be dried before development.

(4) Provided a small trough is used and a reasonably long run is available, pad development is quicker and more economical than winch development.

Soaping Aftertreatment

The fourth and final stage of the azoic dyeing process is still referred to as "soaping", although these days the soap is usually replaced by a more efficient synthetic detergent, of which Lissapol NC is a good example. Its purpose is to change the insoluble pigment on the fabric into the physical state in which it exhibits its best fastness to light and to chlorine, and also to clear away loose pigment which might cause poor fastness to rubbing in the final dyeing. Much has been done and much has been written concerning this soaping treatment, and if little is said about it here that is not because it is unimportant. It is not; it is an essential stage of the azoic dyeing process.

The only point that it is wished to make now is that, however the knitted fabric dyer may regard the other stages of the azoic dyeing process, at the soaping stage he has a decided advantage over the dyer of woven piece goods. The winch is an excellent machine on which to carry out this treatment, as without difficulty the goods can be given—

(*a*) Adequate time—30 min. (repeated if necessary)

(*b*) Adequate temperature—at the boil

(*c*) Adequate liquor—30 : 1 liquor ratio.

In addition, the fabric receives a certain degree of mechanical friction and squeezing as it passes over the winch, and this helps considerably in removing loose pigment.

In sum, although knitted cotton fabric is not the easiest of materials to dye with azoic dyes, if one takes the trouble results can be obtained which, in regard to rubbing fastness at least, will be the envy of the woven piece dyer.

PALE SHADES DYED WITH VAT DYES

A request was received that this paper should also include something about the dyeing of other fast shades on knitted cotton fabric, and for this purpose an item has been selected which may be of interest to those who are concerned more with the dyeing of pale shades than of the heavy azoic shades that have already been discussed. As described in the writer's previous paper[1], a limited range of the Soledon dyes can be used for the production of these pale shades with every satisfaction; but there is a noticeable difficulty in connection with the dyeing of pale blues in that Soledon Blue 2RC, which is the only Soledon which, from a fastness point of view, can be considered for such shades, is not very satisfactory for winch dyeing, mainly owing to its very low affinity for cellulose. In addition, the Soledon dyeing process is generally a two-stage one, and this makes the production of

such shades rather expensive. Attention was therefore directed to the possibility of producing pale shades on knitted fabrics with the normal Caledon dyes, and eventually it was found possible to do this with the aid of a dyeing assistant known as Dispersol VL.

Dispersol VL is a well-known auxiliary product used for the retarding and restraining of the vat dyes when they are applied to cellulose from the normal leuco solutions. With many vat dyes the action of this product is extremely powerful and concentrations of 0·1–0·5 part per 100 of dye liquor are quite sufficient to cause a marked decrease in the exhaustion of the dye and to give a very useful levelling effect. The action of Dispersol VL on the different Caledon dyes is specific, but generally speaking it has the most powerful action on the vat dyes of the dibenzanthrone series, and this is very useful because in general these are the dyes that possess the highest affinity and which give rise to the greatest difficulties when dyeing pale shades.

Over quite a wide range the depression of the equilibrium exhaustion of the vat dyes in leuco form is proportional to the amount of Dispersol VL present in the dyebath, and with some dyes, of which Caledon Jade Green XN is a good example, by increasing the amount of Dispersol VL sufficiently, it is possible almost to inhibit dyeing completely. Generally speaking, however, it is found that by increasing the quantity of Dispersol VL to 10–20 times that normally recommended, the exhaustion can be decreased to approx. 50% of what it would be if no Dispersol VL were present. The effect of this is to change the character of the vat dyebath from one that will give level results with difficulty to one that will readily dye level. Its general behaviour is then, in fact, very much like that of a direct cotton dye.

When dyeing heavy and medium shades, a depression of the exhaustion to 50% of its normal value, although quite feasible technically, is not, of course, a satisfactory economic proposition. Fortunately, when dyeing such shades, this procedure is rarely necessary. It is quite otherwise, however, when dyeing pale shades. These are the cases where a high rate of dyeing and high exhaustion cause considerable trouble when dyeing on the winch in rope form. With such shades, moreover, the amount of dye used is so small that, even if it has to be increased to double the normal quantity in the interest of obtaining level results, then this is by no means unreasonable from an economic point of view. This is in effect what is recommended for the production of such shades with vat dyes, and the general procedure for processing such shades is as follows—

The stock vat is prepared in the normal manner and the dyebath set with the requisite amounts of caustic soda, sodium hydrosulphite, and Dispersol VL. The quantities of Dispersol VL used will vary from 1 to 3 parts per 1000 of dye liquor, and although this is considerably more than is normally recommended, it is not, in itself, an unduly excessive quantity. It is essential however, that the Dispersol VL is added to the dyebath and not to the concentrated stock vat, otherwise the vat dye may be precipitated out of solution. Dyeing is then carried out in the normal manner, adding the stock vat slowly and with dilution to the winch dyebath. It is noteworthy that the increased amount of Dispersol VL will also improve the stability to atmospheric oxidation of the alkaline leuco dyebath. Moreover, with such pale shades, the scumming which very often gives trouble in heavy shades does not exist. When dyeing is complete the dyebath is run off and oxidation carried out preferably with sodium percarbonate or perborate. The goods are then soaped in the normal manner and finished.

Whilst this is a general method, one important point can be stressed: in heavy and medium shades Dispersol VL cannot be used with the Caledon Blues. The solubility of the leuco form of these dyes is generally low, and as the addition of Dispersol VL normally lowers the solubility, these dyes tend to precipitate when Dispersol VL is added to their dyebath. In the case of pale shades the concentration of leuco product present is so low that an addition of Dispersol VL does not cause precipitation. It is therefore quite possible to dye Caledon Blue RC in pale shades, i.e. not exceeding 2% of the S brand by the technique described. This is of considerable importance, because, as already pointed out, Soledon Blue 2RC is not very satisfactory for winch dyeing.

IMPERIAL CHEMICAL INDUSTRIES LTD.
DYESTUFFS DIVISION
DYEHOUSE LABORATORIES
HEXAGON HOUSE
MANCHESTER 9

(*MS. received 18th June 1953*)

Reference

[1] Wiltshire, E. R., J.S.D.C., **62**, 313 (1946).

Discussion

MR. A. P. KERSHAW: Azoic dyes are now in demand for certain Government contracts on knitted cotton. But for general wear, particularly cheap lines like interlock, we find a good deal of customer resistance to the high cost. Has the lecturer found this general?

MR. WILTSHIRE: As far as sports wear is concerned the advantages in fastness of azoic dyes over direct dyes, even when aftertreated, are such that the price factor is not always the major factor affecting their adoption. Ignorance of the best methods of processing has often been the reason why they have not been used.

MR. C. A. MILLS: In the padding of other dyes on circular fabrics, difficulty is often experienced in the form of lines at the double edges of the material. Does not this occur also with azoics?

MR. WILTSHIRE: When developing only on the padding mangle such lines are not obtained. They might be expected to occur if the Brenthol itself were padded.

MR. MILLS: Further to your reply is there not a danger of lack of development at the edges when using Brenthols of low substantivity?

MR. WILTSHIRE: If the cloth is dried before development, then the substantivity of the Brenthol should make no difference in this respect.

MR. J. SAUNDERS: Would the Lecturer give some indication of the critical temperatures in drying before development? Is it essential to have the fabric "bone dry"?

MR. WILTSHIRE: Drying should be carried out with a moderate heat and approx. 5–10% moisture should be left in the fabric. "Bone-dry" fabrics will not wet out easily unless well conditioned before the pad development.

MR. J. DONOVAN: Is there any advantage in applying half the Brenthol, developing, and then repeating the operation to build up the final shade? I have in mind a possible improvement in rubbing fastness and the fact that any uneveness is likely to be masked by the double operation.

MR. WILTSHIRE: Although some improvement in levelness and rubbing fastness might be obtained by this method, it is too cumbersome to be recommended generally.

MR. R. GREENLEES: How long can a diazo solution of the coupling component be kept without fear of decomposition?

MR. WILTSHIRE: The stability varies with the product being used, also with such factors as temperature, pH, and concentration. In a strongly acid condition some diazo solutions are stable for long periods, but generally speaking it is a safe rule to prepare fresh solutions every day.

MR. W. L. LANGTON: Turning to vat dyes, considerable difficulty was experienced during the war in dyeing Jungle Green on interlock. Has this difficulty now been overcome?

MR. WILTSHIRE: Yes. For details of the methods employed reference should be made to the paper already mentioned[1].

MR. T. E. CHARLESWORTH: Has any useful method been evolved to dye a solid shade on a mixture of viscose rayon and cotton with vat dyes?

MR. WILTSHIRE: No general method applicable with all dyes has been entirely successful. Selection of dyes and control of temperature are still the best general principles to follow.

MR. J. SAUNDERS: Owing to the limited range of Brenthols and bases suitable for knitted fabrics, it would appear necessary to use mixtures to obtain certain colours. Has the Lecturer any comment?

MR. WILTSHIRE: Mixtures of Brenthols are permissible but are often difficult to control when feeding up standing baths. Mixtures of developers are not generally advised, as the results obtained are often anomalous in colour and fastness.

A Study of the Afterchrome Process

J. F. GAUNT

Meeting of the West Riding Section held at the Victoria Hotel, Bradford, on 12th March 1953, Mr. S. Peel in the chair; of the Huddersfield Section held at Field's Café, Huddersfield, on 31st March 1953, Mr. E. Rolfe in the chair; and of the Scottish Section, held at the Scottish Woollen Technical College, Galashiels, on 10th December 1953, Mr. R. Graham in the chair

The following aspects of the afterchrome process have been examined—

1. The dyeing of afterchrome dyes prior to chroming
2. The effect of dichromates on wool during afterchroming
3. The effect of dichromates on chrome dyes during afterchroming.

The main difference between chrome dyes and acid dyes of comparable constitution is the greater sensitivity of the former to precipitation by acid. Several of the more commonly used chrome dyes are out of solution under normal dyeing conditions, and yet have excellent level-dyeing properties.

The rate of uptake of chromium by wool during afterchroming is independent of the presence of dye on the wool. When afterchroming at the boil, the pH of the liquor rises steadily, owing to the reduction of chromic acid to neutral tervalent chromium compounds, but this effect is much less marked at 80° and 90°c. The rate of absorption of chromium is very sensitive to the pH of the chroming bath, but is only slightly affected by temperature.

During afterchroming at low pH values, there is a tendency for certain dyes to be destroyed by oxidation. The chrome lakes formed by afterchroming with dichromates have much better wet fastness than those formed by aftertreatment with salts of tervalent chromium.

Prior to the introduction of synthetic dyes during the nineteenth century, almost all colours on wool were produced by mordanting the wool from a solution of a multivalent metal, and then dyeing from a fresh liquor. According to the excellent survey of Giles[1], a wide range of mordants was employed, salts of iron, copper, aluminium, tin, and chromium being in regular use, and from these a large number of colours could be obtained from the relatively small number of natural dyestuffs available. With the development of synthetic dyes, basic and acid dyes which require no mordant became available and enabled dyeings of hitherto unknown brightness to be produced, while new mordant dyes, e.g. Alizarine Orange (1876) and Alizarine Blue (1877), were introduced. For these mordant dyes, the technique of mordanting prior to dyeing was continued, as the insoluble mordant dyes then available had little affinity for unmordanted wool. It was found that dyeing on a chrome mordant gave the best all-round fastness to light and wet processing, and although other mordants give brighter colours with some dyes, e.g. cochineal on tin mordant, the importance of chromium rapidly increased.

The afterchrome process dates from 1887, when Nietzki discovered that Alizarine Yellow 2G (*m*-nitrophenylazosalicylic acid, *C.I.* 36) can be dyed on wool not only on a chrome mordant, but also on unmordanted wool in a similar way to an acid dye, and then converted into the fast chromium complex by adding sodium dichromate to the exhausted dyebath. The afterchrome process requires considerably less time than does dyeing

on a chrome mordant, and as only one liquor is used for both dyeing and chroming there is a saving in steam and water. Furthermore, the fastness of afterchrome-dyed shades is at least as good as those dyed by the chrome mordant process. In view of these advantages, it is not surprising that the importance of the afterchrome process increased very rapidly as the range of suitable dyes expanded, and in spite of later developments in chrome dyeing and premetallised dyes, it is still the most widely used method of dyeing wool in heavy, relatively dull shades where very high wet fastness is required. The first chrome black, Diamond Black F (*C.I.* 299), was first used in 1889, and with the discovery of Diamond Black PV (*C.I.* 170) in 1902 and Eriochrome Black T (*C.I.* 203) in 1904, the importance of logwood, hitherto the most important black for wool, rapidly declined. By 1906, many of the dyes still in regular use for dyeing black, navy, brown, red, yellow, and grey were on the market [2], and by 1914 the afterchrome process had practically ousted the chrome mordant method and had rendered almost all the natural dyewoods obsolete.

Recent work on the theory of the dyeing of chrome dyes has been concentrated on the metachrome process, in which dye and mordant are applied simultaneously. As a result of the work of Stevens, Rowe, and Speakman [3], Schetty [4], Lister [5], and Hannay [6], the mechanism of this process is now well understood and the molecular configuration required for good metachrome dyes, i.e. the ability to exhaust from a neutral dyebath and to combine with chromium, has been in some measure elucidated. As most of the recently introduced chrome dyes are specifically recommended for application by the metachrome process, it appears that the dyemakers have concentrated their interest in mordant dyes on this process.

In spite of this scientific and technical interest in the metachrome process, it cannot be too strongly emphasised that the weight of wool dyed, and particularly the weight of dye used, are far greater by the afterchrome process than the corresponding figures for metachrome dyeing. Attention has been drawn by Stevens, Rowe, and Speakman to the shorter dyeing time of the metachrome process, but the afterchrome method possesses the following outstanding advantages over the other chrome-dyeing processes—

(*a*) *Level-dyeing Properties*— For obtaining dyeings of good wet fastness on fibres other than wool, there are several important methods for after-treating material dyed with dyes of good level-dyeing properties but only moderate wet fastness. Thus, suitable direct cotton dyes can be diazotised and developed, aftertreated with auxiliary products such as Fixanol P (ICI) or Fibrofix (Courtaulds), or with salts of copper and chromium, while certain disperse dyes for acetate rayon can be diazotised and developed. In the case of wool, afterchrome dyeing is the only method by which full advantage can be taken of the excellent level-dyeing and migrating properties of many chrome dyes. The dye can be applied evenly in a similar way to a level-dyeing acid dye and then converted very simply into a much more complicated molecule of high wet fastness. This is not the case with dyeing by the metachrome or chrome mordant processes, in which dyeing and lake formation occur practically simultaneously, so that there is no possibility of migration. Furthermore, to obtain a good metachrome dye which exhausts well from a neutral dyebath, it is necessary to weight the molecule to such an extent that the migrating properties are greatly impaired.

It is, therefore, desirable to ensure that afterchrome dyes should have the best possible migrating properties in the unchromed state consistent with good wet fastness when afterchromed, i.e. that in the unchromed state they should resemble level-dyeing acid dyes rather than the acid milling type. Although greater molecular complexity may be required to obtain the very highest wet fastness, e.g. to potting, such fastness is not essential in the sections of the wool trade dealing with piece and yarn, where level-dyeing properties are of great importance. For these purposes, the existing ranges of suitable dyes leave much to be desired.

(*b*) *Condition of Wool*— It is generally accepted in the wool trade that less damage is done to wool by dyeing from a slightly acid bath than from more strongly acid or alkaline liquors. Support is given to this by the work of Speakman and Coke [7] and of Liu, Speakman, and King [8], who considered that the metachrome process is preferable to other methods of dyeing chrome dyes, as they found a final pH of 5·5 for metachrome dyebaths. This is probably due to the fact that in their work they used open vessels, from which free escape of ammonia was possible, with a consequent fall in the pH. It has since been shown [9–11] that this is not the case in practice, and that the pH of a typical metachrome dyebath rises steadily during the course of dyeing to a value of at least 8. The use of hydrolysable esters in the dyebath [6] enables this rise in pH to be checked, but the pH value recommended by Speakman (pH 5·5) is much closer to that of the afterchrome bath than of a metachrome liquor.

(*c*) *Exhaustion of Dyebath*— By the afterchrome process, good exhaustion even of full shades can be achieved without difficulty by pH control. One of the outstanding disadvantages in metachrome dyeing is the difficulty of exhausting medium and heavy shades.

(*d*) *Cost*— Whilst not important from an academic point of view, it should be noted that it is usually much cheaper to dye any given colours with afterchrome dyes than with metachrome dyes, although in fairness to the latter mention must be made of the superior fastness to light of many of the better members of the range, this being particularly valuable for the paler shades.

Because of the above advantages, the afterchrome process is pre-eminent for dyeing wool in heavy, dull shades, particularly black, navy, maroon, and brown, where very good fastness to wet processing is required. The method is mainly used on loose wool and slubbing, but it is also of importance for cloth and to a lesser extent for yarn.

In view of the very great weight of wool dyed with afterchrome dyes, it is surprising that the theory of the process has received so little attention. In Giles' survey [1] mentioned above, there is no reference to any published work on afterchrome dyeing, whereas several papers on the metachrome process and many on chrome-mordanting, are reviewed.

The details of the procedure for applying dyes by the afterchrome method vary greatly, but the general principle is that the wool is first dyed from a slightly acid bath, the pH of which depends on the dyes employed and on local conditions, and is then treated with sodium dichromate. Chroming is usually carried out in the same liquor as that used for dyeing, although in exceptional cases a fresh liquor may be used. The purpose of the chromium is to combine both with the wool and with the dye, thereby strengthening the link between wool and dye formed during the original dyeing operation. There are obviously a great number of variable factors which require examination, since to the already complex system involved in the acid dyeing of wool is added the further complication of chroming both wool and dye. In the present investigation it has been found convenient to regard the process from the following three broad aspects—

I— The dyeing of afterchrome dyes prior to chroming

II— The effect of dichromates on wool during afterchroming

III— The effect of dichromates on chrome dyes during afterchroming

and these will now be considered individually.

I— The Dyeing of Afterchrome Dyes prior to Chroming

As with all other classes of dyes, the chrome dyes exhibit markedly individual characteristics, particularly as regards their rate of exhaustion under different conditions of pH and electrolyte concentration. Many of them closely resemble acid dyes, the main difference being that the chrome dyes possess the well known groups capable of forming lakes with chromium. In many cases, the only difference between an acid dye and a chrome dye is the presence of a second hydroxyl group in the latter, but this is sufficient to cause the colour of the unchromed dyeing to be extremely sensitive to alkali. The important group of *oo'*-dihydroxyazo dyes, to which belong many of the blue, black, red, and orange afterchrome dyes, give characteristic titration curves from which the two hydroxyl groups can be seen to titrate separately with alkali, the first usually reacting at about pH 7–8 with only a slight change in the colour of the solution, and the second at about pH 9–10, when the colour change is usually sharp and is identical with that which occurs on chroming wool dyed with the dye. This would appear to give further support to the formulæ for the chrome lakes of the *oo'*-dihydroxyazo dyes, in which both the hydroxyl groups are shown as taking part in the lake-formation.

The afterchrome dyes show the same variations in their behaviour towards the pH and electrolyte concentration of the dyebath as do acid dyes, and in general it seems that, whereas increasing the sodium sulphate concentration improves the migration properties and decreases the exhaustion of those dyes which require a low pH (i.e. about 3–4) for good exhaustion, it has little effect on the migration properties of dyes exhausting well at higher pH values, and with such dyes it tends to increase the degree of exhaustion. The same behaviour has been observed with acid dyes, and in both cases it is impossible to make any generalisation regarding the effect of sodium sulphate. The rate of exhaustion is best controlled by selecting the pH conditions which give about 90% exhaustion at the end of the usual dyeing time (i.e. raising to the boil in 45 min. and boiling for 45–60 min.), as shown by Lister [12].

Although the afterchrome dyes are generally similar in dyeing properties to level-dyeing dyes and the less fast members of the acid milling dyes, one interesting and important difference must be mentioned. Solutions of the level-dyeing acid dyes and acid milling dyes in the concentrations used in practice are stable to concentrations of acid considerably greater than those used in a dyebath, but this is not the case with several of the more common afterchrome dyes, which are converted into very fine dispersions, presumably of the free acid, by small amounts of acid. Thus, in a 0·2% solution of Solochrome Black AS (*C.I.* 204) containing 0·06% acetic acid (80%), i.e. equivalent to a 10% dyeing in a 50 : 1 liquor containing 3% acetic acid on the weight of wool, the dye is completely out of solution at 60°C., and dissolves very slowly at 95°C. Similarly, Eriochrome Red B (*C.I.* 652) at 0·08% concentration containing 0·06% acetic acid is out of solution at 40°C., the normal temperature for commencing dyeing, but dissolves quickly as the temperature reaches 65–70°C. Other examples of dyes behaving in a similar way are Eriochrome Orange 2RL (Gy), Omega Chrome Yellow ME (S), Monochrome Red ME (LBH), and Chromoxane Brilliant Red BL (FH). It has also been found that dyes sensitive to low concentrations of acid are often similarly sensitive to sodium sulphate in the concentration used in dyebaths.

This effect is very interesting in that several of the dyes mentioned above are among the most level-dyeing of all chrome dyes, and are in everyday use not only on loose wool and slubbing but also on cloth and yarn where a high standard of levelness is required. Nevertheless, it is highly improbable that they are ever dyed in bulk, certainly in the initial stages of dyeing, except as fine dispersions. The dyemakers' literature often refers to the good solubility of a dye, implying that solubility and level-dyeing properties go hand-in-hand. That this is not so is shown not only by the examples cited above, but by Solochrome Red DS, which has excellent level-dyeing properties and yet is completely insoluble, and also by the disperse dyes for acetate rayon, many of which give very level results on the wool portion of wool–Celafibre blends. While considering the solubility of chrome dyes, the effect of many of the new dyebath

auxiliaries for improving level-dyeing should be mentioned. Many of these, especially those based on non-ionic polyethenoxy compounds or on cation-active substances, cause appreciable aggregation of the dye, and even precipitation if used in excess, and yet are claimed to improve not only the tendency towards skittery dyeing, but also the overall levelness of the material being dyed. In all cases, however, it should be borne in mind that all these insoluble dyes, whether formed by precipitation in the dyebath or by the milling of a naturally insoluble product during the course of manufacture, must be in an extremely fine state of dispersion to avoid filtration on to the wool with the consequent risk of poor fastness to rubbing.

II—The Effect of Dichromates on Wool during Afterchroming

It has already been mentioned that there is very little published information on any of the theoretical aspects of afterchrome dyeing, but the literature on the effect of chromium salts and of dichromates on wool is extensive, although it mainly relates to the chrome mordant process. Kay and Bastow [13] found that when wool is treated at the boil with solutions of sodium dichromate, the liquor becomes alkaline, which was attributed to the wool taking up chromic acid and leaving sodium chromate in solution. The rate of absorption of dichromate was found to be increased by raising the temperature and the acidity of the mordanting bath. Liechti and Hummel's work [14] confirmed many of Kay and Bastow's findings, and paid particular attention to the differences in colour, ranging from yellow to olive and grey, of wool mordanted in presence of different agents. They concluded that the chromium is first taken up by wool in the sexivalent form, and is then reduced by the wool to the tervalent state, possibly through such stages as chromic chromate $Cr_2(CrO_4)_3$. They found that the change in the colour of the wool from yellow to grey begins at 60°C. Carlene, Rowe, and Speakman [15] also showed that at low temperatures the whole of the chromium taken up by wool from chromic acid solutions can be removed in the sexivalent form by a pH 8 buffer solution, whereas when applied at the boil the chromium is rapidly reduced to the tervalent form, which is very firmly held and can be removed only by prolonged extraction with N. oxalic acid. Iljinsky and Kodner [16] noted that the absorption curve of chromic acid and wool is different at temperatures above 60°C. from that at lower temperatures, indicating that reduction commences at this temperature. Bhat and Rao [17] examined the rate of absorption of chromium on various qualities of wool, and found that fine wools take up chromium more quickly than coarse wools at temperatures of 63°C. and 93°C., and that the chromium is absorbed more rapidly from acid than from neutral baths.

In the light of the above, therefore, the effect of boiling solutions of dichromates on wool may be summarised as follows—

(*a*) The chromium is first taken up as chromic acid, by salt formation with basic groups of the wool.

(*b*) The chromic acid is then reduced by the wool to the tervalent state. This leads to an increase in the pH of the liquor, since the strongly acid chromic acid anion is reduced to neutral tervalent chromium, and to maintain electrical neutrality the chromic acid anions are replaced by hydroxyl anions formed by hydrolysis of the water in the liquor.

Although the general theoretical background of chroming is reasonably well understood, little is known of the actual extent to which the above processes operate during practical dyeing, and in the present work the rate and the extent of the uptake of chromium under typical dyebath conditions has been investigated.

It was appreciated that Race, Rowe, Speakman, and Vickerstaff [18] had proved that the rate of absorption of chromium by the tip portions of wool fibres is much more rapid than by the root portions, but since in practice the whole of the fibres are present in the liquor, it was decided to investigate the overall effect. The work to be described was, except where otherwise stated, carried out on 3/13s worsted yarn of 50/56s quality, the tests being made in a 50 : 1 liquor : wool ratio in open Pyrex beakers, using zeolite-softened water with an average alkali content of 40 p.p.m. (as $NaHCO_3$). The yarn was made from soap-scoured wool, and before dyeing was scoured through a five-bowl scouring machine in soap and soda, and then thoroughly rinsed in water, and its total alkali content, as determined by shaking with a known excess of sulphuric acid followed by titration by the pyridine method [19], was 0·5% (as Na_2CO_3). At the end of each experiment, the hank was squeezed through rubber rollers and dried, and the total chromium content was determined by the method of Smith and Sullivan [20]. Preliminary tests on the wool and residual liquor showed that this gave a quantitative return of the whole of the chromium used, and also that the reproducibility of the experiments was sufficiently good to make it unnecessary to employ more precisely controlled conditions.

A—Effect of pH on Rate of Absorption of Dichromate

The method employed was to treat the wool in a liquor containing the requisite assistants, raising the temperature from 40°C. to the boil in 30 min., followed by gently boiling for 30 min. The "bichrome" (potassium dichromate) solution was then added, and boiling continued for the specified time. The pH of the liquor was determined with a Marconi glass-electrode pH-meter, at the beginning and end of dyeing and chroming. Water was added in small amounts throughout the experiments to compensate for the loss of liquor by boiling. Free escape of steam was allowed, although it was realised that this would permit volatilisation of ammonia in the cases where ammonium sulphate was present, but the use of totally enclosed apparatus presents considerable manipulative difficulties and is in any case not representative of most types of bulk practice.

It is essential to know whether the rate and the extent of the uptake of chromium are affected by

the presence of dye on the fibre, and consequently a preliminary set of experiments was made, covering the pH range 3·5–6·5 and amounts of dye ranging from 0·5% to 6%, a parallel experiment without dye being made in each case. The differences in the rate of uptake between the pairs of experiments with and without chrome were so small as to be well within the experimental error, and it was concluded that the uptake of chrome is independent of the amounts of dye encountered in practical dyeing. On the other hand, the pH of the liquor at the commencement of chroming had a marked influence on the rate of absorption of chrome, and it was decided to investigate this in absence of dye, so that visual examination of the patterns could be made for colour i.e. yellowness or greenness, and for uniformity of chroming. The results are shown in Table I.

TABLE I

Rate of Absorption of Chromium during Afterchroming

$K_2Cr_2O_7$ added (%)	Percentage of Chromium absorbed after boiling for (min.)— 5	10	15	30	60	120
No Assistant in Original Dyebath						
0·5	32	36	44	55	72	—
1·0	16	26	28	41	52	63
2·0	7	12	13	17	30	41
4·0	11	16	19	28	36	42
8·0	8	12	16	18	25	31
2% Ammonium Sulphate						
0·5	59	73	82	86	100	—
1·0	29	44	55	80	81	100
2·0	14	24	25	36	41	50
4·0	13	19	20	33	38	59
1% Acetic Acid						
0·5	38	54	59	76	85	—
1·0	27	59	69	82	100	100
2·0	19	26	31	35	45	54
4·0	17	20	23	32	39	51
2% Acetic Acid						
0·5	54	62	85	96	100	—
1·0	49	69	85	100	100	100
2·0	36	41	45	51	54	64
4·0	23	25	30	41	49	60
8·0	14	16	19	21	26	35
1% Formic Acid						
0·5	68	85	97	100	100	—
1·0	68	75	77	93	98	100
2·0	30	32	35	50	63	75
4·0	20	22	28	36	48	57
2% Formic Acid						
0·5	70	85	100	100	100	—
1·0	75	86	89	93	100	100
2·0	47	52	53	65	80	96
4·0	45	47	51	60	65	71
8·0	33	35	39	41	43	47
1% Sulphuric Acid						
0·5	70	82	84	100	100	—
1·0	58	71	75	90	100	100
2·0	41	44	48	57	61	90
4·0	39	40	45	48	55	70
2% Sulphuric Acid						
8·0	48	50	50	52	55	62
4% Sulphuric Acid						
8·0	51	54	60	61	67	71

In the series of experiments with 8% of dichromate, more strongly acid conditions were used, as it was found that the strong buffering properties of the dichromate–chromate system, which were already showing their effect in the series with 4% dichromate, where substantial amounts of chromium remained unexhausted, were masking the effect of the relatively small amounts of acid added to the original dyebath.

From the data given in Tables I and II, the following conclusions may be drawn—

1. The rate of absorption of chromium by wool is governed to a great extent by the pH of the liquor, not only at the commencement of chroming, but also during the chroming operation itself. It is clear that the chromate ions attach themselves to the $-NH_3^+$ ions in the wool arising from the combination of the amino groups of the wool with the acid added to the dyebath. In the case of the experiments in which 0·5%, 1·0%, and 2·0% of dichromate were used to afterchrome wool "dyed" in absence of any assistant, and in which the initial pH of the afterchroming bath was about 7, i.e. well within the isoelectric region, the amount of chromium taken up during the first few minutes is very small and is practically independent of the amount of dichromate added. It appears that under these pH conditions, the number of $-NH_3^+$ groups in the wool is very small.

2. During the progress of chroming, the strongly acid chromate or dichromate ions are reduced to neutral tervalent chromic compounds. Sodium or potassium dichromate can be regarded as a compound of sodium or potassium hydroxide with chromic acid, and if the latter is removed, as during chroming, the system must obviously contain an excess of sodium or potassium hydroxide. This results in a rise in the pH of the liquor as chroming proceeds. Further evidence of this rise in alkalinity has been obtained by taking a number of samples at various stages during bulk afterchrome dyeings. The acid or alkali content of the wool was determined by the pyridine method. In every case, although the wool contained at least 0·5% of acid before chroming, the whole of this was neutralised within the first fifteen minutes of chroming, after which time the wool contained up to 0·3–0·4% alkali. On further boiling, the alkali content decreased as it was neutralised by the dyebath.

3. The proportion of the chromium taken up by the wool is greater when small amounts of dichromate are added, but the total amount absorbed is, as would be expected, considerably greater when more concentrated chroming baths are used. The extent of chroming with the amount of dichromate (ca. 2%) normally used for afterchroming is by no means complete after the customary time of afterchroming (30–60 min.). Confirmation that this is the case in bulk practice has been obtained by determining the chrome content of a large number of samples from commercial afterchrome dyeings. The values were in general about 50–60% of the

TABLE II

Change of pH of Liquor during Afterchroming

$K_2Cr_2O_7$ added (%)	Initial pH	pH of Liquor after boiling for (min.)— 0	5	10	15	30	60	120
			No Assistant in Original Dyebath					
0·5	8·2	7·1	6·7	6·7	6·8	7·9	8·1	—
1·0	8·4	6·9	6·8	6·9	7·2	7·9	8·0	8·2
2·0	8·3	7·0	6·8	7·0	7·3	7·6	7·9	8·2
4·0	8·3	5·8	6·1	6·3	6·4	6·7	7·0	7·2
8·0	8·4	5·6	6·1	6·1	6·2	6·3	6·4	6·6
			2% Ammonium Sulphate					
0·5	7·8	6·8	6·8	6·8	6·8	7·2	7·3	—
1·0	7·9	6·8	6·5	6·6	6·8	7·4	7·4	7·6
2·0	7·9	6·7	6·7	6·7	6·7	7·0	7·1	7·5
4·0	7·7	6·3	6·0	6·1	6·1	6·5	6·5	6·6
			1% Acetic Acid					
0·5	5·0	6·8	6·9	7·1	7·2	7·3	7·3	—
1·0	4·9	6·6	6·5	6·5	7·2	7·5	7·9	8·0
2·0	4·8	6·6	6·5	6·7	6·7	6·9	7·0	7·8
4·0	4·6	5·9	5·9	5·9	5·9	6·4	6·5	6·9
			2% Acetic Acid					
0·5	4·6	6·2	6·6	6·6	6·7	6·8	7·0	—
1·0	4·6	5·1	5·7	5·7	5·7	6·0	6·7	6·7
2·0	4·3	5·0	5·3	5·4	6·0	6·1	7·0	7·2
4·0	4·2	5·4	5·6	5·6	5·6	6·2	6·3	6·6
8·0	4·2	5·1	5·3	5·6	5·7	5·8	5·9	6·1
			1% Formic Acid					
0·5	3·9	5·5	4·9	5·1	5·5	6·0	6·6	—
1·0	3·7	4·6	4·9	5·3	6·0	7·7	7·7	7·8
2·0	3·9	4·8	6·3	6·3	6·4	6·7	7·1	7·5
4·0	3·7	5·4	5·7	5·7	5·8	6·3	6·5	6·8
			2% Formic Acid					
0·5	3·6	4·7	4·7	4·7	4·6	4·7	4·8	—
1·0	3·5	4·1	4·4	4·4	4·5	5·0	5·3	5·3
2·0	3·7	4·0	5·1	5·3	5·7	5·8	6·9	7·3
4·0	3·5	4·2	4·9	5·0	5·6	5·7	5·8	6·3
8·0	3·6	4·4	4·5	4·6	4·7	4·9	5·6	5·6
			1% Sulphuric Acid					
0·5	3·0	5·5	5·1	5·1	5·2	6·5	6·8	—
1·0	2·9	4·0	5·2	5·5	5·7	6·8	6·8	7·0
2·0	2·8	4·0	5·7	5·9	6·2	6·4	6·8	7·2
4·0	3·0	4·0	5·3	5·3	5·5	5·8	5·9	6·3
			2% Sulphuric Acid					
8·0	1·9	2·9	3·0	3·4	3·4	3·7	4·3	4·9
			4% Sulphuric Acid					
8·0	1·6	2·1	2·2	2·4	2·5	2·5	2·8	3·0

amount added to the bath, with slightly higher or lower results which could be accounted for by variations in the pH of the bath or in the duration of chroming.

As mentioned above, this work was carried out on wool which, although treated under dyebath conditions prior to chroming, was not actually dyed, and consequently it has been found possible to observe the colour of the final chromed wool. It has been found that wool chromed at pH values above 6·5, i.e. chromed slowly, is greyish green, but as the pH is reduced and the rate of chroming increased, the wool becomes progressively yellower. It seems probable that the cause of this is that, whereas during slow chroming the chromate is reduced to the tervalent state at approximately the same rate as it is absorbed by the wool, when the rate of absorption is accelerated by making the chroming bath more acid, the rate of reduction is outstripped by the rate of absorption. The wool thus contains unreduced chromate, which gives it its characteristic yellow–orange colour. This chromate can be reduced by boiling the wool, particularly in neutral or slightly alkaline solutions, and the wool then becomes grey–green. Alternatively, exposure to light rapidly brings about reduction, and it has been shown that a marked change in tone can arise if wool dyed to pastel shades with dyes of good light fastness and then chromed for a short time, e.g. 15 min., from an acid liquor, is exposed

to light. The light fastness of the yellow coloration arising from the presence of chromates in wool is about 2 on the B.S. 1006 light fastness scale. This emphasises the danger of fading, particularly in pale and medium shades, which can arise even when chrome dyes of high light fastness are dyed and chromed from an acid bath and insufficient care is paid to the reduction of the chromate present on the wool. On account of the high tinctorial value of chromic acid on wool, only a very small amount is required to give the wool an appreciable yellow coloration.

The above hypothesis regarding the rate of reduction of chromate ions present in wool at different pH values has been investigated on a number of samples by extracting the wool with a pH 8 buffer by the method described by Carlene, Rowe, and Speakman [15]. As was anticipated, no sexivalent chromium can be extracted from the greyish-green wool chromed at the higher pH values, but with yellow patterns the amount of extractable chromate was proportional to the intensity of the yellow colour. In no case, however, did the amount of extractable sexivalent chromium approach that of the non-extractable chromium present on the wool, the maximum proportion of the former being 15% in the case of the pattern treated for 15 min. with 2% dichromate from a sulphuric acid bath.

CHROME MORDANT PROCESS

When applying dyes by the chrome mordant process, it was usual to refer to "reduced", "sweet", and "sour" chrome mordants, of which the first was most suitable for dyes susceptible to oxidation and the last the least suitable [21]. The agents most commonly used for producing reduced chrome mordants were cream of tartar, lactic acid, and tartaric acid, none of which would be expected to reduce dichromates to the tervalent state in solutions of normal dyebath concentration, viz. 0·2–0·4%, even on prolonged boiling. This has been confirmed by refluxing 0·2% solutions of potassium dichromate containing 0·2% of cream of tartar, lactic acid, and tartaric acid respectively for 4 hr. Titration of the final liquors showed that the whole of the chromium was still in the sexivalent state. As none of the above agents used in reduced chrome mordanting baths was strongly acid, the rate of uptake of chrome would be slow, and there would be little unreduced chrome on the wool at any time. In addition, all of them are strong chelating agents for tervalent chromium, which they would tend to remove from the wool, thereby accelerating the rate of conversion of dichromates into tervalent chromium. In "sour" chrome mordanting, the rate of absorption of chromate would be much more rapid and the danger of unreduced chromate on the wool much greater. As mentioned by Horsfall and Lawrie [22], "formic acid has the advantage of completely exhausting the mordanting bath, but care must be taken to obtain even treatment, and the same is probably even more important in the case of sulphuric acid", which the same authors state to be "rather drastic as an assistant".

EFFECT OF WOOL QUALITY

As mentioned above, the experimental work described in this paper was mainly carried out on 50/56s-quality wool, but in view of the fact that the rate of absorption of dyes under identical dyebath conditions is greater on botany than on crossbred qualities, owing to the greater surface area of the former per unit weight, two series of experiments were made to discover whether this is true for the rate of absorption of chromium. The wool qualities used were—

(*a*) 50/56*s*, 3/13*s* worsted counts
(*b*) 58*s*, 4/16*s* worsted counts
(*c*) 64*s*, 2/28*s* worsted counts

The results are shown in Tables III and IV, both of which refer to 2% potassium dichromate in presence of no addition and 2% acetic acid respectively.

The diameter of the fibre has only a slight influence on the rate of absorption of chromium,

TABLE III

Duration of Chroming (min.)	50/56s Wool Initial pH 8·5		58s Wool Initial pH 8·6		64s Wool Initial pH 8·6	
	% $K_2Cr_2O_7$	pH	% $K_2Cr_2O_7$	pH	% $K_2Cr_2O_7$	pH
0	—	6·0	—	6·0	—	6·0
5	7	7·1	8	6·8	10	7·1
10	12	7·3	13	7·1	15	7·1
15	13	7·3	17	7·4	20	7·4
30	17	7·4	21	7·6	24	7·6
60	30	7·7	29	8·0	29	7·7
120	41	8·5	44	8·4	39	8·5

TABLE IV

Duration of Chroming (min.)	50/56s Wool Initial pH 4·3		58s Wool Initial pH 4·0		64s Wool Initial pH 4·0	
	% $K_2Cr_2O_7$	pH	% $K_2Cr_2O_7$	pH	% $K_2Cr_2O_7$	pH
0	—	5·0	—	5·1	—	5·2
5	36	5·3	33	5·7	39	5·7
10	41	5·4	42	5·8	42	5·7
15	45	6·0	46	5·9	46	5·9
30	51	6·1	57	6·0	63	5·9
60	54	7·0	63	6·4	74	6·0
120	64	7·2	86	6·8	88	6·9

but in general finer fibres give more rapid exhaustion than coarser qualities, thus confirming the results of Bhat and Rao [17]. The effect of wool quality on rate of uptake of chromium during the normal period of afterchroming (30–45 min.) is, however, not sufficient to call for any variations in dyeing technique.

CHROMING BELOW THE BOIL

When applying dyes by the afterchrome process, it is common practice at the end of the dyeing process to run away part of the liquor, and then to fill up the dyeing machine with cold water prior to adding the dichromate, thereby obtaining an initial chroming temperature of 80–90°C. It is claimed that this modification of the afterchrome process gives better levelness of the final result. To discover whether any difference in the rate of chroming arises from chroming at temperatures below the boil, two series of tests were made with 2% of dichromate, the wool being "dyed" at the boil as before, and then chromed at 80° and 90°C. respectively. The results are shown in Tables V–VIII.

Comparison of Tables V, VII, and I, and of VI, VIII, and II, which refer to afterchroming with 2% dichromate under different pH conditions at 80°C., 90°C., and the boil respectively, leads to the following conclusions—

1. The inital rate of exhaustion at 80°C. is slightly greater than at 90°C. or the boil, but the amount of chromium taken up at the boil is considerably greater than at 80° or 90°C.

2. At 80°C. the rise in the pH of the liquor is less than at 90°C., which in turn is less than at the boil. This is due to the much lower rate of reduction of the chromium from the sexivalent to the tervalent state at the lower temperatures, so that there is a correspondingly lower rate of build-up of alkali in the liquor. The wool chromed below the boil is much yellower than the corresponding sample chromed at the boil. The amount of sexivalent chromium extracted by a pH 8 buffer is greater at 80°C. than at 90°C., and much greater than at the boil on all the samples examined.

Lister [23] has found that the chromic acid anion ($HCrO_4^-$) migrates readily at 80°C., but not at the boil. This is no doubt due to the fact that at the latter temperature the $HCrO_4^-$ ion is so rapidly reduced that migration in the form of this ion cannot take place. Qualitative tests made during the course of the present work have confirmed this observation. There appears, therefore, to be a sound theoretical basis for beginning the chroming process at 80°C., at which temperature the dichromate can be taken up uniformly by the wool, and then raising to the boil and boiling for 20–30 min., during which time the chromium is reduced evenly throughout the material and converted into the dye–chromium lake.

To sum up, the chroming of wool is a very complex operation, as in addition to the normal adsorption process there are complicating factors—

(*a*) The pH of the chroming liquor changes during chroming, thereby affecting the rate of uptake of chromium during the process.

TABLE V

Rate of Absorption of Chromium during Afterchroming with 2·0% Potassium Dichromate at 80°C.

Original Dyebath Assistants	Percentage of Original Chromium absorbed after treating for (min.)—					
	5	10	15	30	60	120
No addition	5	10	22	28	31	41
1% Acetic acid ...	18	21	24	28	33	42
2% Acetic acid ...	31	37	38	41	49	61
1% Formic acid ...	36	43	44	49	58	61
2% Formic acid ...	61	64	64	65	67	80
1% Sulphuric acid ...	52	52	55	55	55	68

TABLE VII

Rate of Absorption of Chrome when Afterchroming with 2·0% Potassium Dichromate at 90°C.

Original Dyebath Assistants	Percentage of Original Chromium absorbed after treating for (min.)—					
	5	10	15	30	60	120
No addition	6	9	10	12	21	42
1% Acetic acid ...	16	22	23	30	32	39
2% Acetic acid ...	23	30	40	42	45	61
1% Formic acid ...	23	33	37	44	48	56
2% Formic acid ...	50	52	60	61	70	75
1% Sulphuric acid ...	49	49	54	57	62	73

TABLE VI

Change of pH of Liquor during Afterchroming with 2·0% Potassium Dichromate at 80°C.

Original Dyebath Assistants	Initial pH	pH after treating for (min.)—					
		0	5	10	15	30	60	120
No addition	8·3	6·8	6·2	6·2	6·3	6·3	6·7	6·8
1% Acetic acid	4·7	5·8	5·6	5·6	5·6	5·7	6·1	6·1
2% Acetic acid	4·3	4·9	5·0	5·0	5·0	5·0	5·4	5·5
1% Formic acid	3·9	4·5	4·8	4·8	4·9	4·9	5·4	5·6
2% Formic acid	3·6	3·8	3·9	4·0	4·0	4·1	4·3	4·5
1% Sulphuric acid ...	2·9	4·0	3·8	3·8	4·0	4·2	4·3	4·6

TABLE VIII

Change of pH of Liquor when Afterchroming with 2·0% Potassium Dichromate at 90°C.

Original Dyebath Assistants	Initial pH	pH after treating for (min.)—						
		0	5	10	15	30	60	120
No addition...	8·4	7·0	6·4	6 7	6·8	6·9	7·0	7·0
1% Acetic acid	4·7	5·5	6·1	6·1	6·1	6·3	6·4	7·0
2% Acetic acid	4·2	5·0	5·5	5·5	5·5	5·6	5·9	6·0
1% Formic acid	3·8	4·8	5·4	5·5	5·8	5·8	5·8	6·2
2% Formic acid	3·5	4·0	4·5	4·6	4·6	4·7	4·7	5·3
1% Sulphuric acid ...	3·0	4·3	4·9	5·0	5·0	5·0	5·3	5·7

(*b*) The wool is almost certainly chemically damaged by the strong oxidising action of the dichromate, and therefore has progressively greater accessibility to the dichromate as the operation proceeds.

(*c*) The chromic acid combined with the wool is steadily reduced to tervalent chromium, and the rate at which this occurs must affect the actual amount of chromic acid present at any time.

III—Effect of the Dichromate on the Dye already present on the Wool

The purpose of the chroming operation is primarily to convert the dye already present on the fibre into the chromium lake, thereby greatly increasing its wet fastness. Although sexivalent chromium can be stripped from wool without difficulty, even by a cold pH 8 buffer, tervalent chromium is extremely difficult to remove. The link between chrome dyes and tervalent chromium is very strong, as can be shown by the difficulty of removing the chromium from chrome complexes prepared *in vitro*. Furthermore, all chrome dyes in the unchromed state have some wet fastness, which differs between individual dyes. This is due mainly to the salt linkages between the sulpho or carboxyl groups of the dye and the basic groups of the wool, but these salt linkages usually give much lower wet fastness than that of the dye chromed on wool, when the dye is firmly linked to the wool through the chromium.

In this section, various aspects of the chroming of dyes present on wool will be considered.

A—MINIMUM AMOUNT OF CHROMIUM FOR COMPLETE FIXATION OF DYE

The actual composition of the chromium complex formed during afterchroming is not known with certainty. Race, Rowe, and Speakman [24] proved that the type of complex formed from certain *oo'*-dihydroxyazo dyes dyed by the afterchrome process is that containing one atom of chromium to two molecules of dye, and Widmer [25] considers that this type of complex is formed almost invariably by the usual chroming processes.

On the basis of such complexes, it is possible to calculate the minimum amount of chromium to fix a given amount of dye. Assuming a molecular weight of 400 for the dye, that the actual dye content of commercial standard concentrations is 40% and that no unreacted intermediates capable o reacting with chromate, e.g. aminophenols or aminonaphthols, are present, 2000 parts of dye require 0·5 mole (147 parts) of dichromate, i.e. 7·4% on the weight of dye. Laboratory tests have shown that even a full shade (8%) of Solochrome Black WDFA can be made fast to milling by after-treatment with 0·5% dichromate, thus confirming the findings of Crook [26]. In practice, however, this means that all the chromium added to the chroming liquor is exhausted on to the wool, where it is fully reduced and combined with dyes. It is by no means certain that such an ideal state of affairs would arise in practice, especially if the duration of chroming were unduly shortened, so that part of the chromium remained in the liquor. On the whole, therefore, it is advisable to ensure that at least 12–15% of dichromate (on the weight of dye) is present on the wool, and taking into consideration the relatively poor exhaustion of dichromate, a reasonable minimum figure is about 20% of the weight of dye, although an even greater proportion may be required for very tippy-dyeing wools.

B—RESULTS OF UNEVEN ABSORPTION OF CHROMIUM

As shown earlier in this paper, the rate of absorption of chromium during the first few minutes of chroming is very rapid, particularly in strongly acid baths. Visual examination of patterns treated in the laboratory with dichromate from boiling acid liquors shows that the danger of uneven absorption of chromium is much greater than that of uneven uptake of most of the afterchrome dyes, e.g. Eriochrome Red B, Acid Alizarine Black R, Chrome Fast Brown TV, under the same dyebath conditions of pH and electrolyte concentration. In view of the high affinity of chromium on the fibre for dye, the possibility arises that a dyeing which is perfectly level before chroming can become unlevel as a result of uneven uptake of chromium. This has been examined by dyeing 3% Eriochrome Red B from a bath containing 2% acetic acid (80%), raising the temperature from 40°C. to the boil in 30 min., and boiling for 30 min. To the bath were added small patterns (each 1 g.) of the same quality of wool chromed at the boil for 45 min. in separate liquors containing 2% acetic acid (80%) and 0, 0·5, 1, 2, and 5% dichromate respectively. The dyebath containing the dyed and chromed patterns was then boiled for a further 30 min., and at the end of this time visual examination showed that the depth of shade on the various patterns was proportional to the amount of chromium on the wool. Similar results have been obtained with Chrome Fast Cyanine 2B, Diadem Chrome Brown RH, and Solochrome Yellow 2GS. It is evident, therefore, that uneven chroming can cause unlevelness to arise during the last stage of afterchrome dyeing. As the initial rate of absorption of chroming is largely governed by the pH of the liquor, the danger is greatest from strongly acid baths. The pH of the chroming liquor is usually that required to give good exhaustion of the dye, and must, therefore, be a compromise between obtaining sufficient exhaustion of the dye and not exhausting the dichromate too rapidly.

C—EFFECT OF TEMPERATURE ON CHROMING

It has already been shown that the rate of uptake of chromium at 80° and 90°C. is not greatly different from that at the boil, particularly during the first 30 min. of chroming. The rate of reduction to the tervalent form is lower at temperatures below the boil, but is sufficient to give adequate fixation of chrome dyes in 30–45 minutes' chroming. The wet fastness of dyeings afterchromed at 80°C. is satisfactory, but the amount of sexivalent chromium remaining in the wool is so great that it gives the wool a strong yellow colour of poor light fastness. For this reason, chroming at temperatures below the boil could not be tolerated for any but very heavy shades, which can in any case be dyed satisfactorily by the orthodox afterchrome technique.

D—EFFECT OF THE pH OF THE CHROMING BATH ON COLOUR

Mixtures of dichromate and sulphuric acid were formerly used extensively for stripping dyes in the rag trade, on account of their strong oxidising effect. Although the concentrations of chromate and acid used for afterchroming are rarely more than a quarter of that used for chrome-stripping, the danger of appreciable destruction of dye exists with some dyes. With most dyes, the colour produced is practically independent of the pH of the chroming bath, but a few special cases should be mentioned—

(*a*) Morgan and Main Smith [27] showed that Diamond Black PV required oxidation to the quinonoid form to achieve its full fastness and true colour. Only by chroming from a strongly acid bath can this be done, and chroming at higher pH values gives a redder dyeing of inferior fastness. Fortunately, this dye requires a fairly strongly acid dyebath, and although it is usually chromed from a fresh liquor the acid retained by the wool is sufficient to give full development of the colour.

(*b*) Eriochrome Red B is well known to give considerably better colour value when dyed on a chrome mordant than by the afterchrome process, which in turn yields a heavier shade than does the metachrome method. Royer, Millson, and Amick [28] consider the poor metachrome value to be due to the formation in the dye liquor of the chrome lake, which is absorbed preferentially by the tips of the fibres, giving a very skittery result. The danger of complete destruction of this dye is, however, very real, and if an attempt is made to dye this dye from a bath containing dichromate and sulphuric acid instead of metachrome mordant, only a flat yellow is produced. This unexpected shade is not due to precipitated unchromed dye failing to react with the chromate, as it does not give a red coloration on treatment with excess alkali, and it must be due to breakdown of the dye. By using acetic acid instead of sulphuric acid, the colour is similar to that of the afterchrome dyeing of the same dye concentration. A similar, though less pronounced, effect occurs when patterns of wool dyed in the same dyebath with 3% Eriochrome Red B are chromed with 2% dichromate in liquors at different pH values. The colours of the patterns chromed in presence of acetic or formic acid, i.e. with an initial dyebath pH of 3·5–5·5 and an initial chroming pH of 4·5–6·5, are very similar, but in presence of sulphuric acid, i.e. with an initial chroming pH of 3·5, the depth is little more than half that of the other. Microscopic examination of the individual fibres shows that the difference in skitteriness is not sufficient to account for the variation in colour. Similar partial destruction of dye has been observed with other chrome dyes, e.g. Chrome Fast Cyanine 2B, but with the exception of such dyes as Brilliant Alizarine Blue R. which is known to be very susceptible to oxidation, the pH at which serious loss of depth of shade occurs is considerably lower than would normally be encountered in bulk dyeing by the afterchrome process.

Since the experimental work described in this paper was completed, further confirmation of the effect of strongly acid chroming conditions on certain chrome dyes has been given to the present author by Calvert [29]. In this work it was found that on chrome-mordanting wool under various conditions, and then dyeing with a number of typical chrome dyes, the depth of shade was in several cases much less on the wool chromed in presence of sulphuric acid (and therefore containing appreciable amounts of sexivalent chromium) than on the corresponding material chromed from neutral or slightly acid baths. In addition to the case of Eriochrome Red B mentioned above, Calvert found that Monochrome Orange R (*C.I.* 40), Metachrome Brown B (*C.I.* 101), and Solway Blue Black B (*C.I.* 1085) appear to be progressively destroyed as the chromic acid content of the wool increases.

(*c*) Many chrome browns are not fast to carbonising or stoving, both of which cause the colour to be severely affected. The most sensitive dyes, e.g. Chrome Fast Brown TV (Brown RH) (*C.I.* 98) contain free amino groups in positions which cannot conceivably be involved in lake formation, and must therefore be in this form in the chrome lake. It is highly probable that the change in colour during carbonising or stoving arises from conversion of these amino groups into ammonium ions. Neutralisation of the dyed material brings the colour very close to that of the untreated wool, but usually not sufficiently near to avoid unevelness. The amount of acid used in afterchrome dyeing is not sufficient to bring about the marked change of colour occurring during carbonising or stoving, and is in any case usually distributed uniformly throughout the batch. Nevertheless, it has been found in semi-bulk trials that yarn dyed with Brown RH which was level before chroming showed dark patches when afterchromed. This unevenness could be explained either by local oxidation of the dye to the quinonoid form or by sensitivity of the chrome lake to uneven acid distribution, and it has not been possible to obtain definite proof as to which is responsible. As neutralisation caused an improvement in levelness, it is likely that uneven acid concentration was responsible.

Chromium Compounds other than Dichromates

While considering the effect of chromium conditions on the colour of dyes, compounds other than dichromates should be considered. As mentioned above, only tervalent chromium is capable of combining with dyes, and consequently chromium salts, e.g. the acetate or the fluoride, would be expected to be suitable for afterchroming suitable chrome dyes. Chromium hydroxide is taken up by wool without difficulty from dilute boiling solution of chromium acetate or fluoride, and the pH of the liquor steadily falls as the absorption proceeds. When these substances are used for afterchroming they give full development of the colour of all mordant dyes which do not require oxidation prior to lake formation, and with many dyes, especially of the dihydroxyazo configuration, e.g. Eriochrome Red B, Chrome Fast Cyanine 2B, Chrome Fast Black KIT, Monochrome Red ME, the colour produced by afterchroming with chromium fluoride is

much brighter and fuller than that given by dichromate. Unfortunately, as shown by Lister [5], the rate of lake formation with chromium fluoride is much lower than with dichromate, and our own work has confirmed that the wet fastness of dyeings afterchromed with chromium fluoride is much inferior to the comparable dyeings afterchromed in the orthodox way with dichromate. The most probable explanation for this is that the degree of olation of the chromium hydroxide taken up by the wool from solutions of chromium salts is different from that of the freshly reduced chromium hydroxide produced within the wool from the chromic acid absorbed from dichromate solutions. This would lead to a different degree of hydration of the chromium lake, and therefore to differences in the mode of attachment of the lake to the fibre, but the experimental difficulties of establishing the cause of the difference are very great. From a practical dyeing point of view it is clear that, for all-round performance, dichromates are the best of the commercially available agents for fixing chrome dyes on wool.

* * *

The author thanks the Directors of Messrs. Patons & Baldwins Ltd. for permission to publish this paper, and is indebted to Miss L. I. Armstrong for making the determinations of the rate of absorption of dichromate, and to Mr. C. A. W. Beck for making the various dyeing and fastness tests.

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(*MS. received 20th May 1953*)

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Discussion

Dr. R. V. PERYMAN: What components of wool does Dr. Gaunt think are oxidised by chrome?

Dr. GAUNT: In the work described in this paper, no analyses have been made of the amino acids present in wool before and after chroming. By analogy with the effect of other oxidising agents, e.g. hydrogen peroxide, the cystine link appears to be the most likely group to be attacked.

Dr. PERYMAN: The effect of chroming on wool has been investigated in the acid range and no evidence of attack on the cystine sulphur has been found.

Dr. GAUNT: It is possible that the effect of dichromates on wool is dependent on the pH of the liquor, as the oxidation potential of dichromate solutions rises significantly as the pH decreases.

Dr. F. F. ELSWORTH: Whilst investigating the Shinohara method for the determination of the cystine content of wool, it has been found [30] that treatment of the wool with chrome had not resulted in any lowering of the cystine content. This would appear to be evidence against the formation of linkages of the type –S–Cr–S–, since such linkages would be expected to be resistant to hydrolysis and to the action of the reducing agent in the cystine determination, thereby leading to a lower result.

It has also been found that pretreatment of the wool with various reagents can have a pronounced effect on its combination with chrome. Thus, bleaching with hydrogen peroxide, which decreases the cystine content, also decreases the absorption of chrome. We have, in fact, made use of this property as a qualitative test for peroxide-bleached wool. This observation would suggest that the cystine linkage plays a part in the combination between chrome and wool, but it is possible there is another explanation of the effect of peroxide.

Methylation of the wool, on the other hand, has been found to produce a large increase in the amount of chrome absorbed.

Dr. GAUNT: Our own further work confirms Dr. Elsworth's results that there is no significant change in the cystine content (as determined by the Shinohara method) of wool treated with boiling solutions of dichromates at pH values higher than 4. We find, however, that there is a progressive reduction in the cystine content of the wool with decreasing pH of the liquor below pH 4.

Dr. G. H. LISTER: The lecturer's comments on the general position of metachrome dyes are extremely controversial. Peryman's original letter merely drew attention to the possible damage to wool if the pH of the metachrome dyebath rose. The rise in pH is not an essential requirement of the metachrome process, and if steps are taken to control pH then it is probable that no damage will occur.

A number of investigators into this problem have failed to produce any experimental evidence of a decrease in wear properties or tensile strength. This may be due to the fact that, while under normal circumstances a pH of the order of that which arises in an uncontrolled metachrome dyebath may cause damage to wool, when chromates are present there is a potential cross-linking agent.

Although it will be difficult to prove, there does exist some evidence that dyeing with mordant dyes gives rise to a complex of chromium, dye, and cystine link. The catalytic effect of thioglycollic acid in assisting the development of many chrome dyes by means of chromium fluoride is of interest in this respect.

One advantage of metachrome dyes is that they are not precipitated by the mordant in the dyebath and this may be a decided advantage in yarn dyeing even by the afterchrome process.

The lecturer's work on the influence of pH and temperature on adsorption of chromate is extremely interesting. Does he consider temperature or pH as the most satisfactory means of control?

Based upon my own experiences of an investigation of dyeing wool with chrome dyes, it appears to be difficult to generalise and it may be necessary to subdivide the mordant dyes into two groups at least, viz. those which require a certain degree of oxidation before a fully co-ordinated complex is formed, e.g. dyes of the Chrome Black T type, and those which do not require oxidation, e.g. Chrome Red B and Azurole B. However, Dr. Gaunt's work is a really practical start to what is undoubtedly a difficult subject.

Dr. GAUNT: Definite proof of the formation or otherwise of –S–Cr–S– linkages during the chroming of wool would be most valuable in further work on the theory of dyeing. At present, only indirect evidence is available, but it is questionable whether the only absolute proof, i.e. the isolation of an amino acid containing such a cross-linkage, is practicable, as it is likely that the linkage would be destroyed during the preliminary acid hydrolysis of the wool under test. This difficulty of isolating the desired compound applies even more strongly to the question of the chromium–dye–cystine complex.

Although the apparent fibre damage, as assessed by such tests as wet and dry abrasion, during metachrome dyeing is less than that occurring in a buffer solution at the same nominal pH, this cannot be regarded as evidence for the formation of –S–Cr–S– linkages. All pH measurements in such work must be made at temperatures around 20°C., whereas the tests are carried out at the boil, where the pH of the metachrome liquor may well be considerably below that of the buffer solution. Furthermore, the ionic concentration of the buffer solution would probably be appreciably greater than that of the metachrome mordant solution, and would cause more swelling and therefore a greater degree of fibre damage.

As regards the relative merits of pH and temperature control of dyebaths, the former is considered much preferable. It is considerably less difficult to obtain a uniform pH value throughout a dye liquor containing wool, whether as loose wool, yarn, slubbing, or piece goods, than to ensure that the temperature is uniform, especially during the critical period of raising the temperature from the initial stages of dyeing up to the boil. It is well known that the temperature in nearly all forms of dyeing machine can vary by several degrees in different parts of the machine.

Experiments on the Chemistry of Anthraquinone Derivatives

W. BRADLEY

Meeting of the Manchester Section held at the Textile Institute, Manchester, on Friday, 17th April 1953, Mr. F. Farrington in the chair

The results are summarised of work on the chemistry of the anthraquinone vat dyes which has been carried out during the past five years in the Department of Colour Chemistry and Dyeing of the University of Leeds.

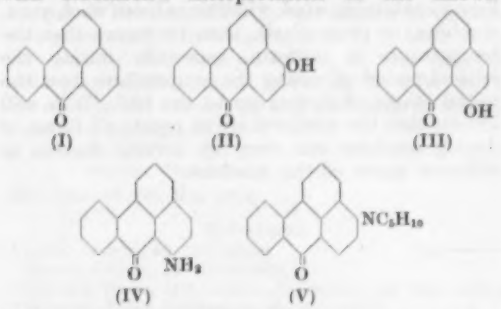
Perkin's synthesis of alizarin from anthraquinone-2-sulphonic acid, sodium hydroxide, and a nitrate or chlorate [1] was more than an important technical and commercial achievement. It set a new problem in theoretical chemistry. Whilst the monosulphonic acids of benzene and naphthalene gave monohydroxy compounds on heating with alkalis, the 2-monosulphonic acid of anthraquinone gave a dihydroxy derivative. In 1901 Bohn [2] observed the formation of indanthrone when 2-aminoanthraquinone was heated with an alkali, and the constitution of the product as established by Scholl [3] indicated that an unexpected kind of aromatic substitution had taken place, the amino group of each of two molecules of 2-aminoanthraquinone having substituted into the nucleus of the other. In 1905 Bally and Isler [4] discovered that two molecules of *meso*benzanthrone condensed together with loss of hydrogen, the dye violanthrone resulting. Other studies, too, in different fields yielded results which could not be accounted for in terms of the theory of the day. Wohl [5] discovered the conversion of nitrobenzene into *o*-nitrophenol by the action of dry potassium hydroxide, and Tschitschibabin [6] observed the formation of *α*-aminopyridine by the action of sodamide on pyridine.

In the early 1920s the whole aspect of the theory of organic chemical reactions was altered by the concepts of Lapworth and Robinson. Lapworth [7] introduced a new classification of reagents and Robinson showed the existence of a new domain of

aromatic chemistry in which the common substituting agents were no longer nitric acid, sulphuric acid, or the halogens, to which we had become accustomed, but the alkali-metal hydroxides, amides, and cyanides, the Grignard reagents, and other reagents capable of providing electrons for the formation of new bonds. The first paper describing the new field [8] appeared in 1932, and much of our recent work at Leeds has consisted in applying to particular problems the basic ideas therein set out.

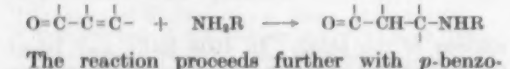
CARBONYL COMPOUNDS

In 1922 A. G. Perkin and Spencer [9] showed that *meso*benzanthrone (I) gave 4-hydroxy*meso*benzanthrone (II) on heating with alkali and an oxidant, and a further study of the reaction [10] showed that the 6-hydroxy derivative (III) was present also. Later work [8, 11, 12], showed that sodamide and oxygen reacted with I to give 6-amino*meso*benzanthrone (IV), and that in the presence of piperidine the product was the 4-piperidino derivative (V). These examples of direct hydroxylation and amination found a ready explanation in terms of theory, indeed they fitted in naturally with Robinson's interpretation of the known

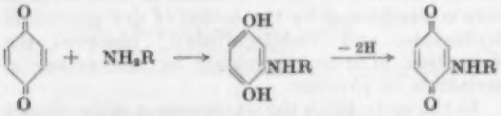


(I) (II) (III) (IV) (V)

ability of $\alpha\beta$-unsaturated ketones and quinones to combine with hydroxides and amines. The simplest reaction occurs with the aliphatic ketones. Here the reagents combine to form a stable adduct, the amine becoming attached to the β-carbon atom of the chain—



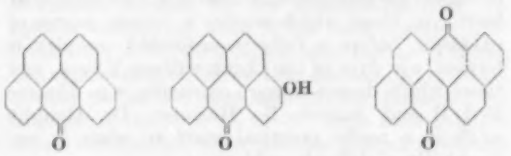
The reaction proceeds further with *p*-benzoquinone, because the first product of addition becomes oxidised by transfer of hydrogen to the unchanged quinone, the two stages taken together leading to substitution in the quinone by the amine—



The amination and the hydroxylation of *meso*benzanthrone follow much the same course, but here it is not possible to differentiate clearly between a stage of addition and one of oxidation.

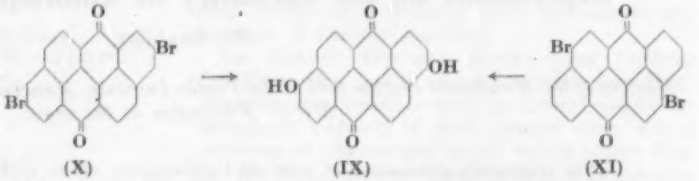
RELATIONSHIP BETWEEN THE NUMBER OF CARBONYL GROUPS AND THE EXTENT OF HYDROXYLATION OF KETONES WITH ALKALI-METAL HYDROXIDES

The initial attack of hydroxyl ions or amines on unsaturated ketones, quinones, or *meso*benzanthrone has its origin in the electron-donating quality of the reagent and the electron-attracting character of the carbonyl group. Once hydroxylation or amination has taken place, a neutralised system results and the ability of the carbonyl group to promote further change is reduced. This result is valid for almost all instances of direct hydroxylation. For example, 1:8:9-naphthanthrone (VI), which we prepared because it contains no fewer than four positions at which hydroxylation might take place, two *ortho* and two *para* to a carbonyl group, affords only a *mono*hydroxy derivative (VII) with potassium hydroxide



(VI) (VII) (VIII)

and manganese dioxide [13]. Under the same conditions anthanthrone (VIII) with two carbonyl groups gives the dihydroxy derivative (IX) [14]. Anthanthrone also reacts with sodamide–morpholine and sodamide–piperidine to give analogous compounds containing two basic groups [14]. How facile is the direct hydroxylation of anthanthrone may be gauged from the fact that both the dibromoanthanthrones (X), (XI) yield the dihydroxy compound (IX) on heating with alkalis. Evidently with each of these compounds the dominant reaction is direct hydroxylation and loss



(X) (IX) (XI)

of hydrogen bromide; the orientation of the resulting dihydroxy compound does not correspond to that of either of the dibromo compounds from which it was derived. The reaction places in a clear light the long-known property of the three monobromophenols, all of which give resorcinol on heating with alkali-metal hydroxides.

THE ACTION OF ALKALI HYDROXIDES AND AMINES ON AROMATIC SULPHONES AND QUATERNARY AMMONIUM SALTS

When instead of carbonyl or nitro groups the nucleus carries electron-attracting groups which do not conjugate with it, neither hydroxylation nor amination takes place. For example, alkyl aryl sulphones and sodamide–piperidine react with decomposition to yield an alkylsulphinic acid and an *N*-arylpiperidine [15]—

$$Ar\cdot SO_3\cdot R + NaNH_2 + NHC_7H_{10} \rightarrow Ar\cdot NC_7H_{10} + NaSO_3\cdot R + NH_3$$

Again, the same reagent breaks down phenyltrimethylammonium iodide to dimethylaniline without nuclear substitution taking place.

THE AROMATIC NUCLEUS AND EASE OF SUBSTITUTION

Although the condensation of amines and hydroxides with benzene derivatives occurs readily enough, analogous reactions occur more easily with naphthalene compounds and still more readily with anthracene. For example, the condensation of piperidine with nitrobenzene occurs readily, but with α-nitronaphthalene it is desirable to employ a diluent [8]. Similarly with carbonyl compounds. Unlike *meso*benzanthrone itself the benzo homologue (XII) readily gives a monohydroxy derivative (XIII) even on heating with alcoholic potassium hydroxide [16]—

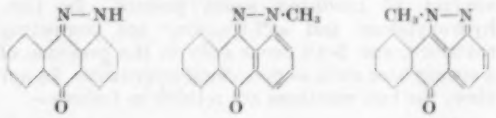
(XII) (XIII)

THE SUBSTITUTING AGENT

The most effective substituting agents are anions which combine most readily with protons, e.g. OH^-, NH_2^-. Un-ionised molecules such as H_2O or NH_3 are incapable of substituting in any but the most reactive nuclei.

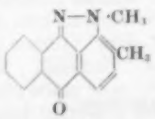
REACTIONS WITH OTHER KETONES

Another ketone which shows the same general character as *meso*benzanthrone is 1:9-pyrazoloanthrone (XIV). It yields two methyl derivatives (XV) and (XVI) having widely different properties [17]. The first is substituted with difficulty,



(XIV) (XV) (XVI)

acetophenone condensing with the nucleus in the presence of potassium hydroxide to form a derivative from which the dimethyl compound (XVII) results on hydrolysis with alkali [18]. It is probable



(XVII)

that the difference in reactivity of the two forms of *N*-methyl derivative is due to the circumstance that XV is a typical aromatic compound whilst XVI has an *o*-quinonoid nucleus. Many other instances could be given in illustration of the same principle: viz. the most reactive of aromatic compounds are those in which the structure deviates most from the symmetry of benzene; in all probability the high reactivity is the result of a low resonance energy.

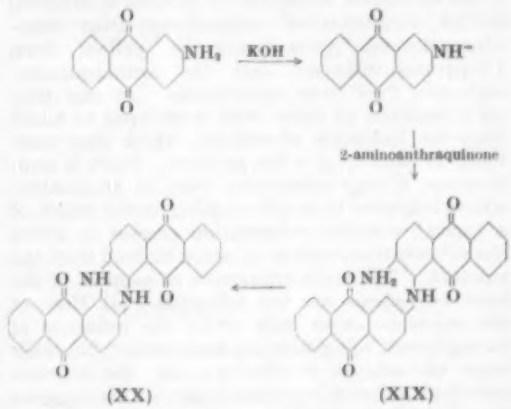
NUCLEAR SUBSTITUTION IN HETEROCYCLIC BASES

The replacement of nuclear hydrogen by hydroxyl ions or amines is not limited to aromatic ketones. The formation of 2-aminopyridine from pyridine and sodamide has been mentioned and we have observed a series of similar reactions with quinoxaline (XVIII), which readily undergoes nuclear substitution with a mixture of sodamide and an amine [19].

(XVIII)

INDANTHRONE AND FLAVANTHRONE

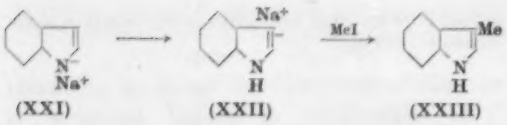
One of the most interesting condensations involving amines is Bohn's preparation of indanthrone from 2-aminoanthraquinone and an alkali. In a detailed study of this reaction we reached the conclusion that the first action of the alkali is to bring about ionisation of the amine, the resulting anion substituting into a second molecule of 2-aminoanthraquinone [20]. The product of such a reaction would be 2-amino-1:2′-dianthraquinonylamine (XIX), and it was shown in separate experiments [21] that this compound could be converted into indanthrone (XX) under a wide variety of conditions, including heating alone, heating in a solvent, or even heating with an acid, e.g. acetic



(XX) (XIX)

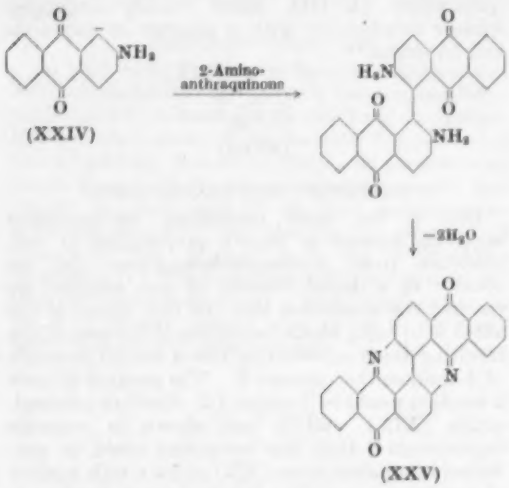
acid. The action of potassium hydroxide on 2-aminoanthraquinone is not limited to ionising the amine. It also substitutes directly into the amine, yielding 2-amino-1-hydroxyanthraquinone. Again, it hydrolyses 2-aminoanthraquinone to 2-hydroxyanthraquinone, and alizarin results from this by direct hydroxylation.

Such an anion as that of 2-aminoanthraquinone can react as though the negative charge were in the nucleus. For example, the methylation of the sodium derivative of indole (XXI) yields a *C*-methylindole (XXIII), and this is understandable only if the original anion changes into XXII. In the same way the anion of 2-aminoanthraquinone should give the carbanion (XXIV), from



(XXI) (XXII) (XXIII)

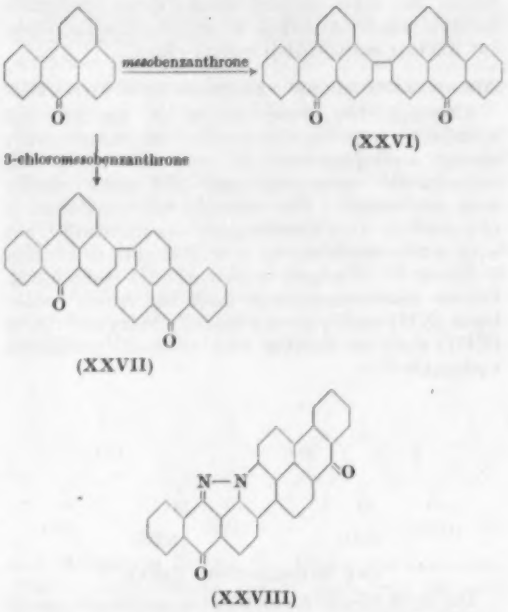
which flavanthrone (XXV) would result following substitution into 2-aminoanthraquinone and loss of water.



(XXIV) (XXV)

THE SELF-UNION OF CARBON COMPOUNDS

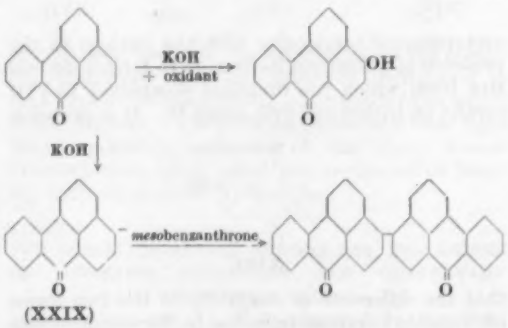
The self-union of carbon compounds is involved in the formation of violanthrone from *meso*benzanthrone, pyrazoleanthrone yellow from 1:9-pyrazoloanthrone, and the anthraquinone-carbazole dyes from anthrimides. At one time such reactions as these were considered to result from the formation of radicals, which then combined in pairs to give the product. There is now, however, a very substantial body of information which indicates that self-coupling is the result of a typical aromatic substitution process in which the substitution agent is an anion derived from the reactant. The main arguments in support of the ionic hypothesis are the following—(*a*) Most of the reactions occur only under the influence of strong bases, e.g. potassium hydroxide. No other form of catalyst is effective, e.g. the reaction *meso*benzanthrone → violanthrone. This suggests a special relationship between the condensing agent and the compound undergoing reaction. (*b*) In many instances the self-coupling reaction occurs side-by-side with a reaction in which an anion substitutes into an aromatic structure, and the relative importance of the two modes of reaction can often be varied at will. (*c*) There are numerous instances where the product of the reaction is not a symmetrical molecule such as would be expected to result from the union of two similar radicals. It is known, for example, that, whilst *meso*benzanthrone yields 4:4′-di*meso*benzanthronyl (XXVI) with sodium anilide in aniline, in the presence of 3-chloro*meso*benzanthrone the product is 3:4′-di*meso*benzanthronyl (XXVII)[22]. Again, in the same category of reactions is the cyclisation of *N*-3-*meso*benzanthronylpyrazoloanthrone to the blue vat dye (XXVIII)[23].



(XXVI) (XXVII) (XXVIII)

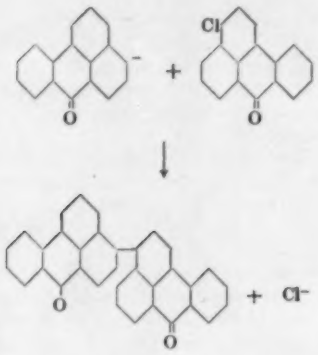
VIOLANTHRONE AND *iso*VIOLANTHRONE

Lüttringhaus[22] showed that 4:4′-di*meso*benzanthronyl (XXVI) was an intermediate in the formation of violanthrone from *meso*benzanthrone. Coupling occurs at a low temperature (110°C.) in the absence of oxidants. At higher temperatures and in the presence of oxidants 4-hydroxy-*meso*benzanthrone (II) is formed, and it is possible to vary the relative proportions of (II) and (XXVI) by altering the temperature and varying the amount of oxidising agent present. In fact, hydroxylation and self-coupling are competing reactions, and both occur only in the presence of a strong base such as potassium hydroxide. In our view, the two reactions are related as follows—



(XXIX)

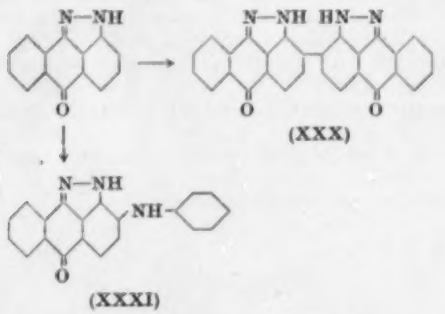
The assumption that the *meso*benzanthronyl ion (XXIX) is formed at an intermediate stage leads to a natural explanation of many unexpected reactions, e.g. the formation of 3:4′-di*meso*benzanthronyl from *meso*benzanthrone and 3-chloro-*meso*benzanthrone already referred to—



and gives a consistent picture of the diverse reactions of *meso*benzanthrone in which alkali-metal hydroxides are used as condensing agents [16].

CHEMISTRY OF 1:9-PYRAZOLOANTHRONE

The formation of pyrazoleanthrone yellow from 1:9-pyrazoloanthrone can be explained in the same way [17]. In this field of work we have employed sodium anilide in aniline as a variant on potassium hydroxide alone or in alcohol, for the reason that aniline is a better solvent than alcohol for compounds of high molecular weight. Sodium anilide and 1:9-pyrazoloanthrone react to give both pyrazoloanthrone yellow (XXX) and 2-anilino-pyrazoloanthrone(XXXI)—



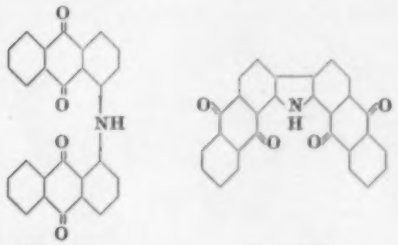
(XXX)

(XXXI)

The reaction is thus entirely analogous to the direct hydroxylation and self-coupling of *meso*benzanthrone brought about by potassium hydroxide. In this investigation we were able to establish that the *N*-methyl derivative (XV) underwent self-coupling with sodium anilide but not with potassium hydroxide, and that the more reactive isomer (XVI) coupled readily with both of these condensing agents. Recently we have made the interesting observation that the Grignard reagent methylmagnesium iodide, a powerful base, causes the self-union of XVI to the corresponding dimethyl derivative of pyrazoleanthrone yellow. On the other hand, the less reactive isomer (XV), though it undergoes self-coupling to some extent also, undergoes substitution by the reagent to give the 2-methyl derivative [18] (XVII). These reactions are of great interest in that they show the common behaviour of potassium hydroxide, sodium anilide, and methylmagnesium iodide, which all behave as strong bases in spite of their various chemical constitutions.

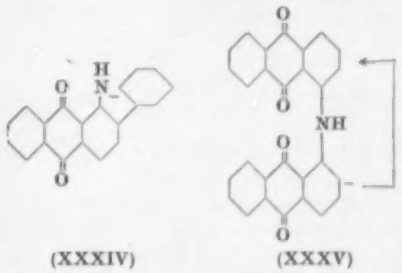
CYCLISATION OF ANTHRIMIDES

In the early years of this century the Farbwerke Höchst showed that useful brown and yellow vat dyes could be produced by the action of potassium hydroxide or aluminium chloride upon 1:1′-dianthraquinonylamine (XXXII). It was later shown that the product was essentially the same whichever condensing agent was used, and that the reaction was a process of dehydrogenation leading to the formation of a diphthaloylcarbazole (XXXIII) by cyclisation [24].



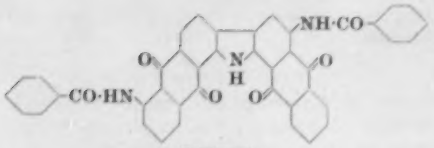
(XXXII) (XXXIII)

We have confirmed the identity of the products obtained by the use of aluminium chloride and potassium hydroxide and also that the structure is correctly given by XXXIII. Thus when potassium hydroxide is used one of the by-products is the monophthaloylcarbazole (XXXIV), and further heating with the same reagent gives a carbazolecarboxylic acid, from which carbazole itself results



(XXXIV) (XXXV)

on distillation with soda-lime. Nowadays the description "carbazole dye" has become widely accepted, but this was, in fact, the first direct demonstration that the carbazole nucleus is present in a so-called "carbazole dye". The mechanism of cyclisation we believe to be analogous to the formation of di*meso*benzanthronyl from *meso*benzanthrone, viz. that the anion (XXXV) is formed under the action of the alkali and then condenses with itself to yield a derivative of carbazole. Our most recent work in this field has been to establish the constitution of the brown vat dye which results by the action of sulphuric acid on 4:5′-dibenzamido-1:1′-dianthraquinonylamine. This product was once considered to be an acridine (*C.I.*1151), but more recent writings have referred to it as a carbazole dye (XXXVI). We have confirmed [25] that the carbazole structure is correct by removing



(XXXVI)

the two benzoyl groups and the two resulting amino groups in turn and showing that the product is the diphthaloylcarbazole (XXXIII).

* * *

In conclusion I should like to thank most sincerely the many researchers who have helped carry on the investigation I have described and whose names appear in the list of references which follows.

(*MS. received 9th June 1953*)

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Discussion

Dr. A. E. STUBBS: When prints of indanthrone and its derivatives are allowed to lie, particularly in a hot, damp condition, before or after ageing, the result is often dull and greenish and does not show some of the reactions of the true dye, e.g. it does not readily green on treating with an oxidising agent. The effect is aggravated by highly alkaline conditions and is still obtained when the reducing agents present cannot yield formaldehyde. Could Professor Bradley suggest what reaction is occurring here?

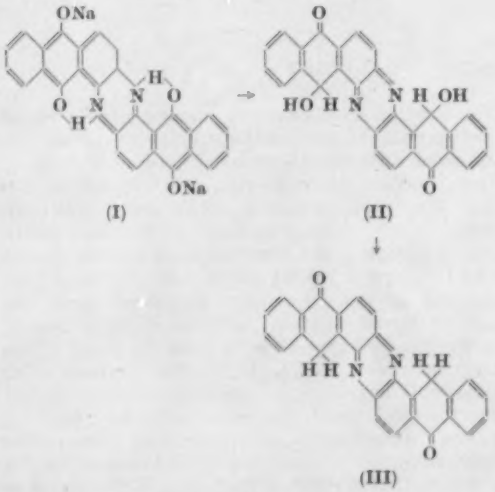
Professor BRADLEY: It is well known that reduced indanthrone is not only easily reoxidised to indanthrone but also is easily isomerised to a derivative (anthrone form) from which indanthrone cannot be regenerated by exposure to air. The isomerisation reaction is hindered by alkalis and cannot underlie the effect referred to by Dr. Stubbs. There is another possibility. We have found that the amine substituent can be detached from 1-amino- and 1-alkylamino-indanthrones by treatment with hydrosulphite and an alkali-metal hydroxide, and the reaction is facilitated by an increase in the concentration and amount of alkali employed. It is possible that under the conditions referred to by Dr. Stubbs opening of the dihydroazine ring takes place accompanied by a change in brightness and hue.

Mr. F. FARRINGTON: Although indanthrone has been known for forty-seven years, and an enormous amount of research has been undertaken to elucidate the theory of its formation, yields are still relatively low.

Professor BRADLEY: I do not know how much work has been done during the last forty-seven years on the mode of formation of indanthrone from 2-aminoanthraquinone. I am quite sure, however, that very little has been published. I believe the lack of success in improving the yield of indanthrone has been due primarily to uncertainty as to the reactions which are involved. Indeed, as I have shown in my lecture, the true nature of the indanthrone synthesis from 2-aminoanthraquinone was recognised only recently.

Mr. H. R. HADFIELD: It is well known that the presence of certain qualities of dextrin in the dyebath prevents the decomposition of leuco-indanthrone. Likewise, leuco-indanthrone absorbed on cellulosic fibres in a blank dyebath decomposes less rapidly than leuco-indanthrone in solution. Can Professor Bradley use his theories to explain these observations?

Professor BRADLEY: I have seen the remarkable protective action of dextrin but I have not had enough experience of it to make my opinion worth while. As regards the enhanced stability of "leuco"-indanthrone on cellulose, chemical change between solids or gases and solids is generally hastened by bringing both into solution. Sorbing "leuco"-indanthrone on cellulose should have the effect of removing the dye from contact with all the dyebath constituents save those in the immediate neighbourhood of the fibre.



(I) (II) (III)

Mr. M. R. FOX: Referring to a question raised by Dr. Stubbs concerning the formation of a reduction- and oxidation-stable green shade of

indanthrone produced under certain printing conditions by the caustic soda method of application, does the author think, that the green could possibly be associated with a tendency to the formation of a more stable azine form by partial loss of hydrogen from the dihydroazine ring? The normal azine is known to be green-yellow, but can be re-reduced with hydrosulphite. There could possibly be present a stable oxanthrone (II) or anthrone (III) of the azine, which originates from the hydrogen-bonded leuco compound (I), but clear evidence of the existence and nature of these products (II and III) is not recorded.

Professor Bradley: As Mr. Fox no doubt has in mind, the dihydroazine ring of indanthrone is stable only so long as an adequate number of carbonyl groups remains. If all the carbonyl groups are reduced and the "leuco"-indanthrone is still in contact with the reducing agent, a change to the azine structure seems unlikely. If after reduction, however, the reduced dye is exposed to air, it appears to be quite possible that formation of the azine ring will occur and that the product will be stabilised by the bond-formation shown in Mr. Fox's formula I. The further change of I into II and III appears to be quite feasible.

PUBLICATIONS SPONSORED BY THE SOCIETY'S FASTNESS TESTS CO-ORDINATING COMMITTEE—XIII

Investigations into Fastness to Perspiration—II

Perspiration Fastness Subcommittee

In the first report [1] an account was given of the work of the subcommittee dealing with fastness to perspiration, up to September 1952. It had been found that natural perspiration was very reactive with certain dyeings on cotton which contained copper, introduced either during the manufacture of the dyes themselves or by aftertreatment with copper salts. The reaction consisted in removal of the copper and it was found that of all the constituents of natural perspiration, histidine was the most reactive in this way. Subsequent work has dealt with a further examination of this effect.

The dyes first examined and mentioned in the first report were Chloramine Sky Blue FF(*C.I.*518), Solar Red Brown 2RL and Coprantine Orange 2BRL, the blue and orange being aftertreated with copper sulphate and the red–brown being a copper-complex dye. The copper, in dyeings of all three, is very readily removed by natural perspiration, and it was obviously necessary to ascertain if the ease of removal of copper is peculiar to them or if it is common to copper-containing dyeings in general. It was also important to examine both wool and cotton dyes, and to discover if chrome-complex dyes on wool are similarly affected.

WOOL DYES

For tests on wool the following were selected—

(i) An acid grey mixture
(ii) 1·5% Erio Fast Purple A
(iii) 2·0% Neolan Blue 2G
(iv) 2·0% Neolan Green B
(v) 1·0% Irgalan Grey BL

The acid grey mixture (i) was a combination of—

0·54% Alizarine Direct Blue AR (IG)
0·22% Azo Rhodine 2G (C.I.31)
0·22% Xylene Light Yellow 2G (C.I.639)

the blue being selected because of its very good fastness to salt.

Erio Fast Purple A contains copper and the remaining dyes are chrome-complex dyes.

Patterns dyed as above were sewn on to a long strip of cotton cloth and the whole worn as a body belt, the patterns being next to the skin. In addition they were tested by the "S.D.C. Plate Method" at 38°C., using the following solutions—

1. A.A.T.C.C. solution at pH 5.
2. A.A.T.C.C. solution at pH 8.
3. S.D.C. solution at pH 5.
4. S.D.C. solution at pH 8
5. As 3 but with addition of 1 : 1000 histidine hydrochloride.
6. As 3 but with addition of 3 : 1000 histidine hydrochloride.
7. As 4 but with addition of 1 : 1000 histidine hydrochloride.
8. As 4 but with addition of 3 : 1000 histidine hydrochloride.

It can be said at once that practically no change in colour was produced by either the natural or the artificial testing methods with three of the dyes, but changes were observed with the green and the acid grey mixture. Neolan Green B treated with natural perspiration exhibited very little or no change to the yellow side but with all the artificial solutions became perceptibly yellower. The reason for this is not apparent. The acid grey mixture showed a slight change to the blue side but this was evidently a pH effect, causing migration of the red and yellow, as it was most marked with the artificial tests carried out at pH 8.

It was necessary to ascertain what effect, if any, these treatments had on the light fastness as it seemed possible, particularly with Erio Fast Purple A, that they might produce some depreciation. However, daylight exposures disposed of this possibility as there was no material difference in fastness between the untreated patterns and those treated with either the natural or artificial solutions. There did appear to be a slight lowering of the light fastness of the acid grey mixture when treated with natural perspiration and also with the solutions containing histidine but the effect was hardly sufficient to be conclusive. It thus appears that the marked effect of natural perspiration on certain dyes does not occur with wool but is

Table I

Light Fastness of Aftercoppered Dyeings (except Solar Red Brown 2RL) treated with Natural Perspiration and with Artificial Test Solutions

	Untreated	Natural	A.A.T.C.C.		S.D.C.		Histidine 1:1000		Histidine 3:1000	
	pH 5	pH 8	pH 5	pH 8	pH 5	pH 8	pH 5	pH 8	pH 5	pH 8
Solar Red Brown 2RL ...	6–7	4–5	6–7	6–7	6–7	6–7	4–5	4–5	4–5	4–5
Chloramine Sky Blue FF (Aftercoppered) ...	5	2–3	3	2	4	4	1	1	1	1
Cuprophenyl Red BL	5–6	4	4–5	4–5	5	5	4	4	4	3
Coprantine Bordeaux 2RLL ...	6	5	5–6	5–6	6	6	5	5	5	4–5
Chlorazol Copper Blue FB ...	5	2–3	5	5	5	5	2–3	2–3	2–3	2–3
Cuprophenyl Navy RL ...	6–7	5	6–7	6	6–7	6–7	5	5	5	5
Cuprofix Brown CBL	5	3	4–5	4–5	5	5	3	3	3	3
Cuprofix Brown C3BL ...	5–6	4	5–6	5–6	5–6	5–6	4	4	3–4	3–4
Cuprofix Grey CRGL	5	3	4–5	4–5	5	5	3	3	3	2–3

confined to the cellulosic fibres. A more extended examination has been made of direct cotton dyes aftertreated with copper sulphate alone and with certain fixing agents containing copper.

Aftertreated direct dyeings

There are on the market today a large number of fixing agents for direct dyes some of which can be applied in conjunction with copper salts and some of which contain the copper either as admixture or as a metal complex. Tests have been made with Cuprofix S and Resofix CU as representatives of this group and dyeings of the following dyes aftertreated with these two products and also with copper sulphate alone have been examined in a similar manner to the wool dyes mentioned above. In addition 1% Solar Red Brown 2RL and 1% Chloramine Sky Blue FF (aftercoppered) were included as controls.

2·0% Cuprophenyl Red BL
3·0% Coprantine Bordeaux 2RLL
2·0% Chlorazol Copper Blue FB
4·0% Cuprophenyl Navy RL
3·0% Cuprofix Brown CBL
3·0% Cuprofix Brown C3BL
1·0% Cuprofix Grey CRGL

It must be noted that the natural perspiration tests were made by wearing patterns next to the skin as before and not by using perspiration collected as in the original S.D.C. work on the subject [2] and therefore cannot be expected to produce quantitative results. They are rather an indication of general effect (Table I). As the results of these tests are of considerable importance each dye will be considered separately.

Chloramine Sky Blue FF (Aftercoppered)

As found previously, natural perspiration causes the colour to become less green in tone, obviously a reversion towards the uncoppered colour, and, as a result of the removal of copper, a considerable reduction in light fastness. With the S.D.C. solution at both pH 5 and pH 8 the colour became slightly less green and the light fastness was slightly affected but with the A.A.T.C.C. solutions the change in colour was much like that with natural perspiration, particularly at pH 8. All the solutions containing histidine gave a marked change, more than was produced by the natural test used for comparison, but the latter might have given a more drastic alteration with longer treatment.

Solar Red Brown 2RL

The colour of this dyeing became orange with natural perspiration, with lowering of light fastness; with the S.D.C. solution at both pH 5 and pH 8 there was no material alteration and with the corresponding A.A.T.C.C. solutions only a slight change to the yellow side. With neither of these artificial tests was there any effect on light fastness.

All the tests made with histidine gave the change to orange with lower light fastness, the difference between these results and those with natural perspiration being that histidine gave a clearer shade.

Cuprophenyl Red BL

The aftercoppered colour became less fast to light when treated with natural perspiration but became only slightly bluer. The S.D.C. solution had practically no effect and the A.A.T.C.C. solution caused a slight drop in light fastness (less than with natural perspiration), neither result being influenced by the pH value. The solutions containing histidine all gave a result very similar indeed to that produced by the natural test. The effect of pH was again negligible except with the solution containing 3 : 1000 histidine at pH 8 which had the most effect, giving a depreciation in light fastness greater than that with the particular natural test made.

The results obtained with patterns aftertreated with Cuprofix S and Resofix CU were almost duplicates of those with the aftercoppered dyeings, again the solutions containing 3 : 1000 histidine at pH 8 being most reactive. The normal S.D.C. solution in these cases gave a very slight lowering of light fastness, if anything more marked at pH 8 than pH 5, but the A.A.T.C.C. solution gave a noticeably less fast colour, rather more pronounced at pH 8, although it had less effect than natural perspiration.

Coprantine Bordeaux 2RLL

With this dye, natural perspiration caused the colour of the aftercoppered dyeing to become bluer with a lowering of the light fastness, both being very closely imitated by the S.D.C. solutions containing histidine but not with either the normal

S.D.C. or A.A.T.C.C. solutions. The pH did not affect the result.

The Cuprofix- and Resofix-treated dyeings behaved very similarly.

Chlorazol Copper Blue FB

With all three aftertreated dyeings treatment with natural perspiration gave rise to a marked diminution of the light fastness which was not imitated by either the normal A.A.T.C.C. or S.D.C. solutions. However, all the solutions containing histidine gave almost identical results which did not appear to be influenced by pH.

Cuprophenyl Navy RL

In this case the effect of natural perspiration was to cause the colour to become a little greener, with some lowering of the fastness to light. It was closely imitated by the solutions containing histidine but not by the A.A.T.C.C. or S.D.C. solutions. Again differences in pH did not appear to influence the result.

Cuprofix Brown CBL

The aftercoppered dyeing became slightly brighter when treated with natural perspiration and this was imitated by the solutions containing histidine at pH 5 and, to a rather less extent, at pH 8. With these solutions, as with natural perspiration the light fastness was lowered and to about the same extent. The normal S.D.C. solution had no effect on either colour or light fastness but the A.A.T.C.C. had some effect on the colour at pH 5 and gave a slight depreciation in light fastness at both pH 5 and pH 8. This depreciation was considerably less than that produced by natural perspiration.

Cuprofix-treated dyeings behaved similarly.

Cuprofix Brown C3BL

All three methods of aftertreatment gave similar results in that the colour became a little bluer with natural perspiration with lowering of light fastness, and these results were closely imitated by the solutions containing histidine. Actually, in the series under review, the artificial solutions had more effect on the light fastness than the natural test but as mentioned earlier the natural test was not carefully controlled.

Neither the normal S.D.C. nor A.A.T.C.C. method gave comparable results.

Cuprofix Grey CRGL

Once again there was no difference in the behaviour of the three aftertreated dyeings, which became slightly redder when treated with natural perspiration and considerably less fast to light. A very similar result was produced by the solutions containing histidine but the normal S.D.C. solution was without effect. The A.A.T.C.C. solutions gave an effect somewhat similar in character to that of natural perspiration but only to a slight extent.

The above tests show that the effect of natural perspiration on dyeings containing copper is not confined to those cases where the copper is known to be relatively loosely combined with the dye, e.g. Chloramine Sky Blue FF aftercoppered, but appears to be general throughout the range of direct dyes which are applied by the usual after-coppering process and also when aftertreated by means of fixing agents containing copper. The tests also indicate that the present S.D.C. and A.A.T.C.C. tests for fastness to perspiration are by no means satisfactory, as they do not produce results which are in any way comparable with those given by natural perspiration. On the other hand, if to the normal S.D.C. solution an addition of 1 : 1000 histidine hydrochloride is made, its effect on these dyes will closely imitate that of natural perspiration. This effect of histidine does not appear to be markedly influenced by variation in pH value.

COPPER-COMPLEX DIRECT DYES

There remained one further type of direct dye which it was necessary to examine, viz. the type containing copper as a metallic complex. For this purpose the following were chosen—

1·5% Chlorantine Fast Yellow 2GLL
1·5% Chlorantine Fast Violet 5BLL
2·0% Chlorantine Fast Blue 2RLL
2·0% Durazol Blue 2GNS
2·0% Solar Turquoise Blue GLL
2·0% Solophenyl Brown BL
2·0% Solar Brown PL
2·0% Solophenyl Grey 4GL

Patterns dyed with these dyes were worn next to the skin for a fortnight under conditions of moderately heavy perspiration in the manner given earlier and were then tested for fastness to light in comparison with—

1. An untreated pattern.
2. Patterns treated by the S.D.C. solution at pH values of 5, 7, and 9 respectively.
3. Patterns treated by the S.D.C. solution with addition of 1 : 1000 histidine hydrochloride at pH 5, 7, and 9 respectively.

The three pH values were selected as it was considered that they would completely cover the range likely to be found with natural perspiration.

Throughout these tests the normal S.D.C. solution did not produce any effect on the light fastness at either pH value, although in every case natural perspiration did, but the effect of the histidine-containing solutions was disappointing. The results were as follows:—

Chlorantine Fast Yellow 2GLL

Some depreciation in light fastness with histidine solutions at pH 5 but less than with natural perspiration, less at pH 9, and none at pH 7. This result would seem to be anomalous but it does indicate that the histidine solution is appreciably less severe in its action than natural perspiration.

Chlorantine Fast Violet 5BLL

With natural perspiration the colour becomes slightly redder and the light fastness much lower. The histidine solutions gave, if anything, a slightly bluer shade and the light fastness was only slightly lowered.

Chlorantine Fast Blue 2RLL

The effect of natural perspiration was to give a flatter and appreciably redder shade of considerably inferior light fastness, while the histidine solutions had only a very small, if any, effect.

Durazol Blue 2GNS

Natural perspiration caused very little alteration in tone but a lower light fastness. The histidine solutions had only a very small effect, that at pH 9 being greatest.

Solar Turquoise Blue GLL

Here again the histidine solutions caused a slight lowering of the light fastness but to a less extent than natural perspiration, the most severe effect being at pH 5.

Solophenyl Brown BL

In addition to depreciating the light fastness, natural perspiration gave a somewhat blacker colour. The histidine solution at pH 9 gave a slightly blacker colour, less so than with natural perspiration, but only a slight effect on the light fastness; at pH 5 there was less alteration in colour but the light fastness was more affected although less than with natural perspiration.

Solar Brown PL

Natural perspiration caused the colour to become a little more orange in tone but this was not imitated by the artificial tests. The latter, however, did bring about a lowering of the light fastness but not to quite the extent of the natural test.

Solophenyl Grey 4GL

Here the effect of natural perspiration was most marked, the very good fastness to light of the untreated dyeing becoming poor and at the same time the colour became a little redder. Both these effects were produced, but to only a small extent, by the histidine solutions, there appearing to be rather more effect at pH 5.

From these tests it was apparent that the addition of 1 : 1000 histidine to the standard S.D.C. perspiration solution did not convert the latter into a satisfactory artificial testing solution as it was much less drastic than natural perspiration in its action on these copper-complex dyes.

A further point was the change in colour brought about by natural perspiration with Lumicrease Blue 2RL and Solar Grey 4GL which the histidine solutions did not imitate or only to a slight extent. This change in colour was similar to that caused by acid conditions and therefore the pH value of the naturally treated patterns was examined. It was found to be 4·5.

Further tests were therefore made with two solutions at pH 4, these containing 3 g. common salt and 1 g. and 5 g. respectively histidine hydrochloride per litre. One gram of the latter gave a pH value of a little above 4, and the required pH was obtained by a small addition of tartaric acid. In the case of the solution containing 5 g. histidine hydrochloride it was first neutralised with sodium carbonate and then brought to pH 4 by adding tartaric acid. pH 4 was chosen deliberately to exaggerate somewhat any effect of the acidity found with natural perspiration. It was realised that the amount of histidine present in the stronger solution was largely in excess of the amount of amino acids present in natural perspiration but the effect of natural perspiration is in many cases a cumulative one and the active ingredients may be present on the material in a much higher concentration than in the perspiration itself. The treated patterns were exposed to daylight alongside an untreated pattern, a naturally treated dyeing not being included as the amount available was very limited; the fading which occurred could therefore be compared with the fading of the latter in a general way only. The results of tests made on dyeings of six dyes are given below.

Chlorantine Fast Violet 5BLL

Considerable fading occurred with 5 g. histidine per litre but not as much as with natural perspiration although of similar character. Slight fading occurred with 1 g. histidine per litre, this being similar to the result in the previous tests.

Chlorantine Fast Blue 2RLL

Neither artificial test imitated the colour change produced by natural perspiration and neither gave as much depreciation in light fastness. There was noticeable fading with the 5 g./l. histidine solution and a slight amount with the 1 g./l., the latter being similar to previous tests.

Solar Turquoise Blue GLL

Both artificial solutions caused the colour to become greener, an effect not noticeable with natural perspiration but the 5 g./l. solution gave a similar depreciation in light fastness to the latter; the 1 g./l. solution had a smaller effect on the light fastness.

Solophenyl Brown BL

The 5 g./l. solution closely imitated the effect of natural perspiration but the 1 g./l. solution was not sufficiently reactive.

Solar Brown PL

The 5 g./l. solution imitated fairly well the effect of natural perspiration both as regards alteration in colour and lowering of light fastness. The 1 g./l. solution was not sufficiently severe.

Solophenyl Grey 4GL

Again the 5 g./l. solution gave a similar colour change to that produced by natural perspiration and lowered the light fastness by nearly as much. The 1 g./l. solution had little effect on the light fastness.

These tests demonstrated fairly clearly that the amounts of histidine which were found to be adequate when dealing with dyeings produced by aftertreating with copper salts or products containing copper were not satisfactory with dyeings dyed with copper-complex dyes; with these an amount approximating to 5 g./l. was necessary.

A final series of tests was made using solutions containing the following—

Table II

Light Fastness of Dyeings treated with Natural Perspiration and by Testing Methods using Histidine

	Untreated	Natural	5:1000 Histidine pH 4	Histidine pH 7	Hydrochloride pH 9
Chlorantine Fast Violet 5BLL	5–6	3	3	4	4–5
Chlorantine Fast Blue 2RLL	5–6	3	3–4	4	4
Solar Turquoise Blue GLL	6	5	5	5	5
Solar Brown PL	5	4	4	4	4
Solophenyl Brown BL ...	6	4	4	4	4
Solophenyl Grey 4GL ...	5–6	2	2–3	3	*

* Shade badly affected by the treatment

(*a*) 3 g. Common salt and 5 g. histidine hydrochloride per litre at pH 4.

(*b*) 3 g. Common salt and 5 g. histidine hydrochloride per litre at pH 7.

(*c*) 3 g. Common salt and 5 g. histidine hydrochloride per litre at pH 9.

(*d*) 3 g. Common salt and 1 g. histidine hydrochloride per litre at pH 4.

(*e*) 20 g. Common salt and 5 g. histidine hydrochloride per litre at pH 4.

The object of this last test was to ascertain if an excessive amount of salt would produce a colour change similar to that given by natural perspiration.

In addition to these, tests were carried out at pH 7, with 3 g. per litre common salt and 5 g. per litre glycine and four other amino acids which are present in natural perspiration, viz. arginine hydrochloride, L-leucine, lysine hydrochloride, and DL-valine respectively. Daylight exposures were made of patterns treated in these various ways in comparison with untreated patterns and patterns exposed to the action of natural perspiration.

The tests were carried out using the S.D.C. Plate Method [3], as laid down in the Second Report of the Fastness Tests Committee (except for the variation in the solutions employed), and were made on dyeings of six dyes, and with the following results—

The tests confirmed that the solution containing only 1 g. per litre histidine hydrochloride was not sufficiently drastic in its action. It was concluded that it need not be considered further. The effect of increasing salt concentration was inconclusive; in general it did not markedly affect the colour but there were indications that it might lessen the depreciation in light fastness.

Of the amino acids other than histidine, in the concentration used, glycine was the most active with four of the dyes but with Chlorantine Fast Blue 2RLL and Solophenyl Brown BL, DL-valine gave rather more fading. The other three amino acids generally gave rather less fading. Comparing the effect of glycine or DL-valine, whichever was more reactive, with the results obtained with histidine, the latter gave the greater effect with Solar Turquoise Blue GLL, Solophenyl Brown BL, Solar Brown PL and Solophenyl Grey 4GL, was about equal with Chlorantine Fast Violet 5BLL, and less severe with Chlorantine Fast Blue 2RLL. These results are therefore largely confirmation of earlier work which indicated that of all the amino acids known to be present in human perspiration, histidine is the most reactive in removing copper from copper-containing dyeings.

The effect of histidine compared with natural perspiration is given below for each dye examined, and the effect on the light fastness in Table II.

Chlorantine Fast Violet 5BLL

At pH 4 histidine gave the most fading and at pH 7, if anything, a little more than at pH 9. At pH 4 the fading was not quite as severe as with the naturally treated pattern and was also redder in character. Neither of the solutions exactly imitated the colour of the latter.

Chlorantine Fast Blue 2RLL

Again the most fading occurred with the pattern treated at pH 4 but this was not as great as with the naturally treated pattern nor was the effect on the colour the same.

Solar Turquoise Blue GLL

All three histidine solutions gave a similar degree of fading, at least as much as given by natural perspiration. At pH 4 the colour became greener, an alteration not noticeable in the other cases.

Solar Brown PL

All three histidine solutions gave similar fading, rather more than with natural perspiration and a similar but not quite identical change in colour.

Solophenyl Brown BL

The three histidine solutions gave practically identical fading, slightly more than with natural perspiration but did not imitate the blackening of shade produced by the latter.

Solophenyl Grey 4GL

All three histidine solutions caused a reddening, more so than with natural perspiration. Also, at pH 9 there appeared to be some destruction of dye. Fading was very pronounced in all cases, being slightly the most at pH 4 at which it was nearly equal to that with natural perspiration.

Conclusion

The Subcommittee believe that their work has established a new principle in that it has shown that natural perspiration can have a profound effect on dyeings produced with copper-complex

direct dyes or with direct dyes which have been aftertreated with copper-containing products and that this effect is due to removal of the copper. (That this is by no means of purely theoretical interest is proved by the number of instances of fading of garments in actual wear which have been traced to this cause.)

The active ingredients in producing this result are amino acids and of all those known to be present in human perspiration histidine has been found to be the most reactive.

The copper in such dyeings is largely responsible for their high light fastness and it necessarily follows that removal of copper must lead to a depreciation of this fastness.

The subcommittee do not know of any artificial testing solution for perspiration so far put forward which can be considered to imitate the above effect of natural perspiration and consider the present methods inadequate.

Although the effect of natural perspiration has not been imitated precisely in the present investigation it is believed that the information obtained provides a basis for a greatly improved test.

(*Received 11th November 1953*)

References

[1] Investigations into Fastness to Perspiration, J.S.D.C., **68**, 392 (1952)

[2] Report of the Fastness Committee in fixing standards for Light, Perspiration and Washing (Society of Dyers and Colourists, Bradford 1934) p. 19.

[3] Second Report of the Fastness Tests Committee (2nd edition, Bradford 1950. Society of Dyers and Colourists), p. 5.

COMMUNICATIONS

The Dyeing of Acetate Rayon with Disperse Dyes
I—Aqueous Solubility and the Influence of Dispersing Agents
II—The Relation between Aqueous Solubility and Dyeing Properties

C. L. BIRD

Aqueous solubilities have been determined at 25° and 80°C. for a range of purified disperse dyes. The solubilising effect of a number of dispersing agents has been examined. It is shown that aqueous solubility has some bearing on the rate of dyeing of disperse dyes and largely governs their levelling power. Addition of a dispersing agent to an acetate rayon dyebath reduces the percentage exhaustion to an extent which is proportional to the degree of solubilisation.

INTRODUCTION

The most important colouring matters for cellulose acetate rayon are the disperse dyes, which consist mainly of azo and anthraquinonoid compounds. Yellows, oranges, reds, and bordeaux are included in the azo series, whilst the anthraquinonoid compounds include oranges, reds, purples, violets, and blues. In addition, a bright greenish yellow is given by 3-methoxybenzanthrone (Duranol Brilliant Yellow 6G) (XLIII)*, whilst some yellows and yellowish oranges are provided by derivatives of nitrodiphenylamine.

Although a few of these dyes show slight solubility at dyeing temperatures (75–85°C.), they cannot be applied from aqueous solution in the usual way. Instead they are used in the form of very fine dispersions with a particle size of about 2 μ. Disperse dyes are usually sold as powders, which are prepared by milling the press cake with an equal weight of a suitable auxiliary product and a little water, drying, and then mixing with a diluent, e.g. Glauber's salt, to give a product containing 15–40% of actual dye. The auxiliary product used to facilitate grinding may consist of the sodium salt of a cresol-naphthalene-sulphonic acid–formaldehyde condensate together with a little sodium alkylnaphthalenesulphonate [1].

In dyeing acetate rayon with disperse dyes the requisite amount of commercial dye is mixed with water and the concentrated dispersion added to the dyebath through a fine sieve to remove any coarse particles or aggregates of dye. Dyeing is then carried out, the temperature being first raised gradually from 40° to 80°C. and then kept at 80°C.

None of the usual electrolytes is included in the dyebath during application of disperse dyes, but a dispersing agent (1–2 g./litre) is almost always added. The function of the dispersing agent is to promote levelling and, in particular, to prevent surface deposition of dye, which results in poor fastness to rubbing and "specking", which arises from small particles of dye adhering to the surface of the material. These particles are at first invisible, but on storage they "dissolve" in the material to produce coloured specks, which are particularly noticeable in pale shades [2].

The dispersing agents commonly used comprise soap, Turkey Red oil, synthetic detergents of the alkyl sulphate or alkarylsulphonate type, and

* Roman numerals refer to Table I

TABLE I

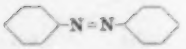
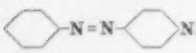
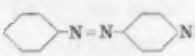
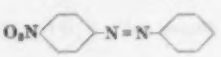
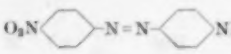
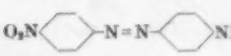
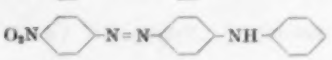
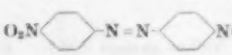
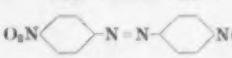
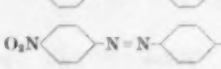
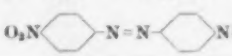
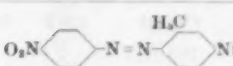
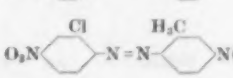
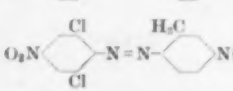
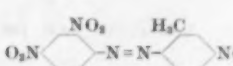
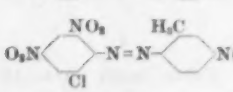
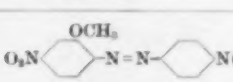
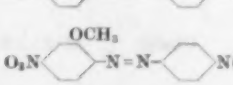
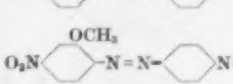
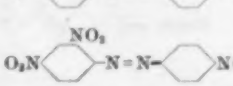
No.	Compound	Mol. Wt.	M.p. (corr.) (°C.)	Colour on Acetate Rayon	Aqueous Solubility (mg./litre)		Solubility in 1% Purified Lissapol LS at 25°C.	
					25°C.	80°C.	mg. per litre	milli-mol. per litre
I		182	68	Yellow	5	—	400	2·2
II		197	124	Yellow	32	330	1120	5·7
III		225	117	Yellow	0·3	8	128	0·57
IV		227	134–135	Dull yellow	<1	13	70	0·31
V*		242	215	Orange	0·3	9·5	42	0·17
VI		256	206	Red-orange	<0·1	2·3	26	0·10
VII*		318	158	Orange	<0·1	0·5	41	0·13
VIII		270	232–234	Red	<0·1	0·2	5·5	0·02
IX		297	151	Red	<0·1	0·2	15	0·05
X*		314	163	Red	0·3	7	138	0·44
XI*		330	206–207	Red	0·4	18	88	0·27
XII*		344	160	Red	1·2	35	610	1·8
XIII*		378·5	187–189	Bluish red	0·2	5	245	0·65
XIV		413	146–148	Brown	1·0	13	455	1·1
XV		389	188–190	Red-violet	0·5	18	255	0·66
XVI		423·5	183–185	Blue-violet	0·2	5·5	165	0·39
XVII†		300	172–173	Red	<0·1	1·6	39	0·13
XVIII†		327	138–139	Red	<0·1	1·2	59	0·18
XIX*		360	154–155	Red	7·1	240	970	2·7
XX†		342	160–161	Violet	<0·1	0·3	23	0·07

TABLE I—*continued*

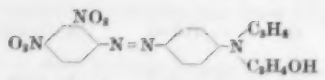
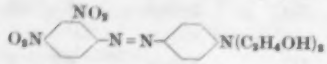
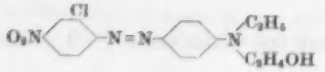
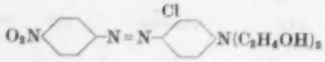
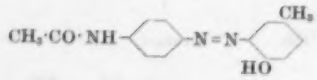
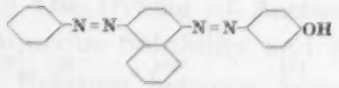
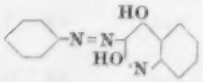
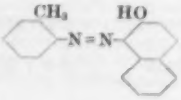
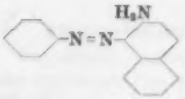
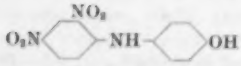
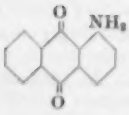
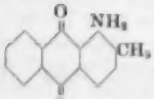
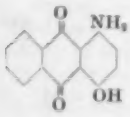
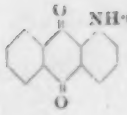
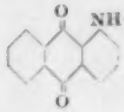
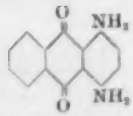
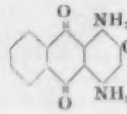
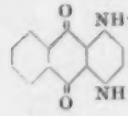
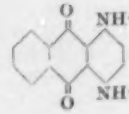
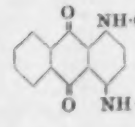
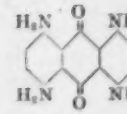
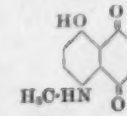
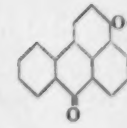
No.	Compound	Mol. Wt.	M.p. (corr.) (°c.)	Colour on Acetate Rayon	Aqueous Solubility (mg./litre)		Solubility in 1% Purified Lissapol LS at 25°c.	
					25°c.	80°c.	mg. per litre	milli-mol. per litre
XXI		359	144–145	Violet	0·6	12	295	0·82
XXII*		375	169–171	Bluish red	2·1	62	345	0·92
XXIII*		348·5	135–136	Bluish red	0·1	5	112	0·32
XXIV*		364·5	189–190	Red	0·7	21	290	0·80
XXV*		269	196–197	Yellow	1·2	17	276	1·0
XXVI*		352	167–168	Yellow–orange	<0·1	0·2	—	—
XXVII*		251	265 (uncorr.)	Yellow	0·6	>20	68	0·27
XXVIII	 (Orange OT)	262	129–130	Orange	<0·2	0·2	82	0·31
XXIX	 (Yellow AB) C.I. 22	247	103	Yellow	<0·2	1·9	340	1·4
XXX*		275	195	Yellow	6·0	108	216	0·79
XXXI		223	251–252	Yellow-brown	0·4	9	275	0·12
XXXII*		237	205	Orange	<0·2	6·5	35	0·15
XXXIII*		239	210–211	Bluish red	0·2	7·5	46	0·19

TABLE I—*continued*

No.	Compound	Mol. Wt.	M.p. (corr.) (°c.)	Colour on Acetate Rayon	Aqueous Solubility (mg./litre)		Solubility in 1% Purified Lissapol LS at 25°c.	
					25°c.	80°c.	mg. per litre	milli-mol. per litre
XXXIV*		237	167	Red	<0·2	5·5	25	0·11
XXXV*		267	173	Red	4·4	43	204	0·76
XXXVI*		238	262 (uncorr.)	Violet	0·3	17	17	0·07
XXXVII*		268	241	Red-violet	0·4	11	65	0·24
XXXVIII*		266	221	Blue	<0·2	2	14	0·05
XXXIX*		326	244–245	Blue	1·2	35	115	0·35
XL*		328	148	Blue	<0·2	<0·2	26	0·08
XLI*		268	>300	Blue	0·9	6	—	—
XLII*		298	>300	Blue	<0·2	<0·2	4	0·01
XLIII*		260	175	Yellow	<0·2	1·2	22	0·09

* Commercial dye † Obsolete commercial dye

fatty alcohol–ethylene oxide condensates. It is not generally known which type of product is most suitable for the purpose, and one aim of the work described in this paper was to discover which products are the most efficient, besides determining the nature of their dispersing action.

It was clear at the outset that the dispersing action of these compounds was bound up with their ability to solubilise water-insoluble dyes. The phenomenon of solubilisation, first described by the McBains [3], is now well known, and the considerable literature relating to this topic has recently been surveyed by Klevens [4]. The simplest picture is that of Hartley [5], who considers that the oil-soluble dye dissolves in the spherical micelles of paraffin-chain salts, the interior of which resembles a minute hydrocarbon droplet. Other workers envisage a sandwich type of micelle, but the idea of solution of hydrophobic dye molecules in micelles is generally accepted. In confirmation of this view it has been found that, in many cases, little solubilisation occurs below the critical concentration at which micelle formation takes place. The solutions obtained as the result of solubilisation are stable, optically clear, and often deeply coloured, i.e. they have the appearance of true solutions.

Rayon dyeing is among the list of industrial processes which Green and McBain [6] (1947) considered would be affected by the process of solubilisation, and in 1949 a group of workers in the United States [7] showed that considerable solubilisation of three purified disperse dyes takes place in 1% solutions of various dispersing agents at 25°C.

In Part I of the present work a much larger range of dyes has been examined, in order to determine aqueous solubilities at 25° and 80°C. and the amount solubilised by 1% solutions of purified Lissapol LS (ICI) at 25°C. A smaller range of dyes was chosen for more extensive study, using a number of commercial dispersing agents. In addition, the effect of increasing the concentration of dispersing agent up to 5 g. per litre at 80°C. has been examined, using various dispersing agents and a single dye, viz. purified Dispersol Fast Scarlet B (ICI).

In Part II some of the results obtained in Part I are compared with the results of levelling tests on acetate rayon at 80°C.

EXPERIMENTAL

Purification of Dyes

The majority of the compounds listed in Table I were obtained through the kindness of British Celanese Ltd., I.C.I. Ltd. (Dyestuffs Division), Williams (Hounslow) Ltd., and the Yorkshire Dyeware & Chemical Co. Ltd., but, as indicated in Table I, by no means all of them are commercial dyes. After removal of dispersing agent with hot water, when necessary, they were recrystallised twice from a suitable solvent, activated charcoal being added in the second recrystallisation. The azobenzene (I) and dimethylaminoazobenzene (III) were AnalaR (B.D.H.) compounds and were not purified further. 4-Nitroazobenzene (IV) was prepared by the method of Angeli and Alessandri [8] and recrystallised from ethanol. XV and XVI were prepared by the author by diazotising 2:4-dinitroaniline and 6-chloro-2:4-dinitroaniline, respectively, in concentrated sulphuric acid and coupling with *NN*-bis-*β*-hydroxyethyl-*m*-toluidine. XXXII and XLIII consisted of small samples of purified dye kindly supplied by I.C.I. Ltd. (Dyestuffs Division).

Purification of Lissapol LS

The commercial compound was first left in contact with acetone at room temperature for 24 hr. to remove any unsulphonated fatty material; after removal of the acetone it was recrystallised twice from ethanol. Analysis of the product by the method of Barr, Oliver, and Stubbings [9] gave mol. wt. 475 (theoretical mol. wt. for sodium oleyl-*p*-anisididesulphonate is 489).

Determination of Solubility in water and in Solutions of Dispersing Agents

The method consisted simply in leaving a small quantity (ca. 0·01 g.) of the crystalline dye in contact with 50 ml. of water or a solution of dispersing agent. One series of experiments was carried out in Vaselined, glass-stoppered, conical flasks which were kept for one month with daily shaking in an incubator maintained at 25°C. The other series was carried out at 80°C. in rubber-stoppered bottles partly immersed in a thermostat bath, the time allowed to reach equilibrium being 24 hr. in the case of solutions of dispersing agents and three days with aqueous solutions. The flow of water in the bath produced slight agitation of the carrier holding the bottles.

The figures for aqueous solubility at 25°C. were checked by means of a parallel series of experiments in which a solution of the pure dye was first allowed to cool from 100°C. Good agreement between the two series was obtained. Experiments showed that three days at 80°C. were sufficient for the attainment of equilibrium, except with XXVII. In the presence of dispersing agent dissolution is more rapid, and experiments with IX and X by F. Manchester (private communication) indicated that 24 hr. are sufficient, and that longer periods are undesirable owing to the tendency of some dispersing agents to hydrolyse.

At the end of the experiment 5 ml. of the solution was withdrawn through a tightly-packed cotton wool plug*, made up to 50 ml. with acetone and the concentration measured by means of a Hilger Spekker photoelectric absorptiometer. Since the cotton wool adsorbed some of the dye, it was necessary to discard the first 5 ml. drawn through the filter, after which little further adsorption of dye by the cotton took place. With the more concentrated solutions of dispersing agents it is important to avoid using a large excess of solid dye, otherwise the results obtained are too high. It is essential that the dye should be visibly crystalline, otherwise solid dye is carried through the filter by the dispersing agent. Since this fault

* Considerable suction is required to draw the solution through the tightly-packed plug. Entry of saliva is prevented by inserting a loose plug of cotton wool in the top of the pipette.

39th Annual CONFERENCE

COLOUR AND TEXTILES

SCARBOROUGH

8th–11th June, 1954

THE TEXTILE INSTITUTE
jointly with the
SOCIETY OF DYERS & COLOURISTS

The 39th ANNUAL CONFERENCE *of the Textile Institute is to be held jointly with the Society of Dyers and Colourists to discuss*

COLOUR AND TEXTILES

The Conference will open on Tuesday, June 8th with a paper on "Changing Standards of Design and the effect on Textiles, with particular reference to Colour"

by

GORDON RUSSELL C.B.E., M.C., R.D.I., F.S.I.A.,
(*Director, Council of Industrial Design*)

Other papers to be presented include :

Technical Limitations to Availability of Colouring Matter

T. VICKERSTAFF, M.SC., PH.D., A.R.I.C., and
E. ATHERTON, B.SC. (*Imperial Chemical Industries Ltd.*)

Specification and Labelling of Colour-Fastness for Consumers

Dr. VAN DER HOEVE (*Nico ter Kuile & Zonen, Enschede, Holland*)

The Use of Coloured Fibres in Yarns

H. BEEVERS, F.T.I., (*Lecturer in Textiles, Bradford Technical College*)

Dyeing of Yarns and Fabrics containing Mixed Fibres (I)

J. S. WARD, B.SC., and
R. C. CHEETHAM, A.R.I.C., A.M.C.T. (*Courtaulds Ltd.*)

Dyeing of Yarns and Fabrics containing Mixed Fibres (II)

R. A. McFARLANE (*Courtaulds Ltd.*)

Fugitive Tinting

W. MEITNER, PH.D., F.T.I., (*British Rayon Research Association*)

Vertical and Horizontal Organisation

W. CROSSLEY (*Yorkshire Dyeing & Proofing Co. Ltd.*)

Spun-Coloured Fibres and Yarns

E. BUTTERWORTH, F.T.I., and
A. S. CLULEY, F.T.I. (*Courtaulds Ltd.*)

Colour and Design in Knitwear

J. C. H. HURD, F.T.I. (*Leicester College of Technology*)

Colour and Design in Woven Fabrics

ALASTAIR MORTON (*Morton Sundour Fabrics Ltd.*)

TIME TABLE

TUESDAY	June 8	Registration from 9 a.m. ; Inaugural Session 3 p.m. ; Assembly (evening)
WEDNESDAY	June 9	Conference Sessions 10 a.m. and 3 p.m. Ladies' Tour (afternoon) Textile Institute Annual Dinner and Dance (evening)
THURSDAY	June 10	Conference Sessions 10 a.m. and 3 p.m. Tour to York (afternoon) Civic Reception (evening)
FRIDAY	June 11	Conference Sessions 10 a.m. and 3 p.m. Ladies' Tour (afternoon) Theatre Visit (evening)

SOCIAL EVENTS

TUESDAY	June 8	Assembly. The Presidents and Officers of the Institute and Society will be glad to meet members and visitors to the Conference at the Grand Hotel.
WEDNESDAY	June 9	Ladies' afternoon tour to Pickering, Goathland and Whitby (tea at Mallyan Spout Hotel). The Institute's 39th Annual Dinner and Dance will be held at the Grand Hotel. All attending the Conference are invited to participate.
THURSDAY	June 10	Afternoon tour to York. In the evening there will be a Civic Reception by the Mayor and Mayoress at the Olympia Ballroom, Scarborough.
FRIDAY	June 11	Ladies' afternoon tour to Troutsdale and Ravenscar (tea at the Raven Hall Hotel). In the evening there will be a visit to the Fol-de-Rols Concert Party at the Floral Hall.

EXHIBITION. It is hoped to arrange an exhibition of fibres and fabrics, in the South Lounge of the Grand Hotel.

GOLF. Ganton Golf Club have offered to provide facilities.

ACCOMMODATION AND FEES

Members of the Textile Institute and of the Society of Dyers and Colourists are warmly invited to attend the Conference. Visitors from overseas will be particularly welcome. Special facilities are available for students. Non-members are also welcome on payment of the appropriate fees.

The Conference will be centred on the Grand Hotel, Scarborough, and Conference Sessions will be at the Spa Theatre.
Accommodation has been reserved provisionally at the Grand and Royal Hotels for 400 visitors.

The Institute cannot guarantee to secure hotel reservations on bookings received after May 10 but every effort will be made to assist those who for any reason cannot book before that date.

It will not be possible to make any refund of conference or other fees in the case of cancellations received after May 10.

The inclusive charge at the Grand and Royal Hotels ranges from 30/- to 42/6 a day Every effort will be made to reserve accommodation of the type required.

Children can be accommodated at both hotels ; a reduction of one-third is made when children under 10 share rooms with parents.

Bona-fide students may attend on payment of a reduced conference fee. Those wishing to do so should, on their booking forms, secure the signature of the Principal of their University or College.

The following fees are payable ; remittances should accompany booking forms :

Members of the Textile Institute and/or of the Society of Dyers and Colourists	£2 2 0
Non-Members	£3 3 0
Bona-fide full-time students	£1 1 0
Lady accompanying Conference visitor	10 6
Ladies' Afternoon Tour, Wednesday (including tea)	10 0
Annual Dinner & Dance, Wednesday	£1 10 0
Tour to York, Thursday	7 6
Ladies' Afternoon Tour, Friday (including tea)	10 0
Theatre Visit, Friday	6 0

A booking-form is enclosed. It will be appreciated if those proposing to attend will complete and return this as soon as possible.

It will help greatly in making arrangements for the Annual Dinner if members will indicate on the booking form with or near whom they would care to sit at dinner.

RESERVATIONS WILL BE DEALT WITH STRICTLY IN THE ORDER IN WHICH THEY ARE RECEIVED

BOOKING FORM

MEMBERS ARE ADVISED
THAT IT IS ESSENTIAL
TO
BOOK EARLY

THE TEXTILE INSTITUTE—39th ANNUAL CONFE

jointly with THE SOCIETY OF D

BOOKING

1. **HOTEL**
Please indicate what you require by filling in below with crosses.

Name of Hotel	Per Day		Single Bed	Twin Bed	Double Room	Nights of June 8th	9th	10th	11th	Private Bathroom if Available (at extra charge)	Extra Nights required to be Booked (Dates)
GRAND	30/- to 42/6	A									
		B									
		C									
ROYAL	30/- to 42/6	A									
		B									
		C									

A = 30/- — 33/- | B = 33/- — 37/6 | C = 40/- — 42/6

A reduction of one-third is made in respect of children up to 10 years of age when sharing rooms with parents or friends.

2. Name/s (Block letters) .....

.....

..... Nationality .....

(Please state titles—Mr., Mrs., Dr., etc. and Degrees)

Address (for receiving preprints and programmes and for the compilation of an attendance list)

.....

.....

DELEGATES REQUIRING SINGLE ROOMS WILL BE ACCOMMODATED WHEREVER POSSIBLE. IF IT IS NECESSARY FOR DELEGATES TO SHARE A TWIN BEDDED ROOM THEY WILL BE NOTIFIED.

DELEGATES REQUIRING EXTRA NIGHTS ARE ASKED TO MAKE THEIR RESERVATIONS AS EARLY AS POSSIBLE. RESERVATIONS WILL BE DEALT WITH STRICTLY IN THE ORDER IN WHICH THEY ARE RECEIVED.

PLEASE INDICATE IF MEMBER OF THE TEXTILE INSTITUTE OR THE SOCIETY OF DYERS AND COLOURISTS

T.I.	
S.D.C.	

CONFERENCE—SCARBOROUGH 8th—11th JUNE 1954
OF DYERS AND COLOURISTS

ING FORM ●

3. Please reserve tickets as below. I enclose fees for the purpose indicated.

CONFERENCE FEE

Member	at £2 2 0	.....
Non-Member	at £3 3 0	.....
*Bona-Fide Student...	at £1 1 0	.....
Lady accompanying Delegate	at 10 6	.....
.....Tickets for Ladies' Tour, Wednesday, June 9 at 10/-		.....
†.....Tickets for Dinner and Dance, Wednesday, June 9 at £1 10 0		.....
.....Tickets for Tour to York Thursday, June 10 at 7/6		.....
.....Tickets for Civic Reception, Thursday, June 10 (No charge)		.....
.....Tickets for Ladies' Tour, Friday, June 11 at 10/-		.....
.....Tickets for Theatre, Friday, June 11 at 6/-		.....
TOTAL		.....

†Annual Dinner Seating. I would like seats for the Annual Dinner next to or near

.....

Cheques etc., made payable to the Textile Institute and crossed, should accompany this form which should be returned to the GENERAL SECRETARY, THE TEXTILE INSTITUTE, 10, BLACKFRIARS STREET, MANCHESTER 3.

SIGNATURE .....

*Signature of Principal of University or College :

.....

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HOTEL .....

ROOMS.....

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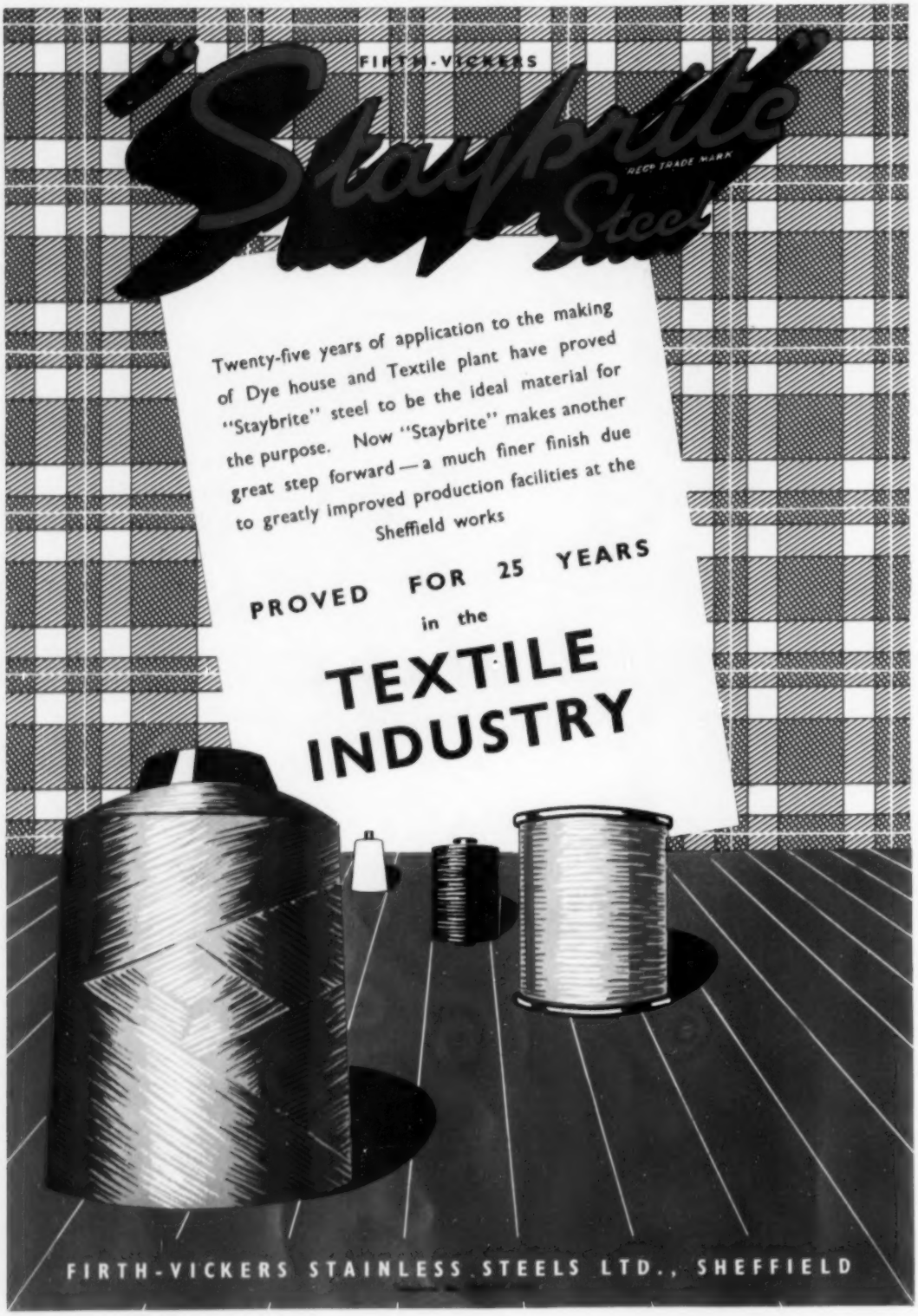
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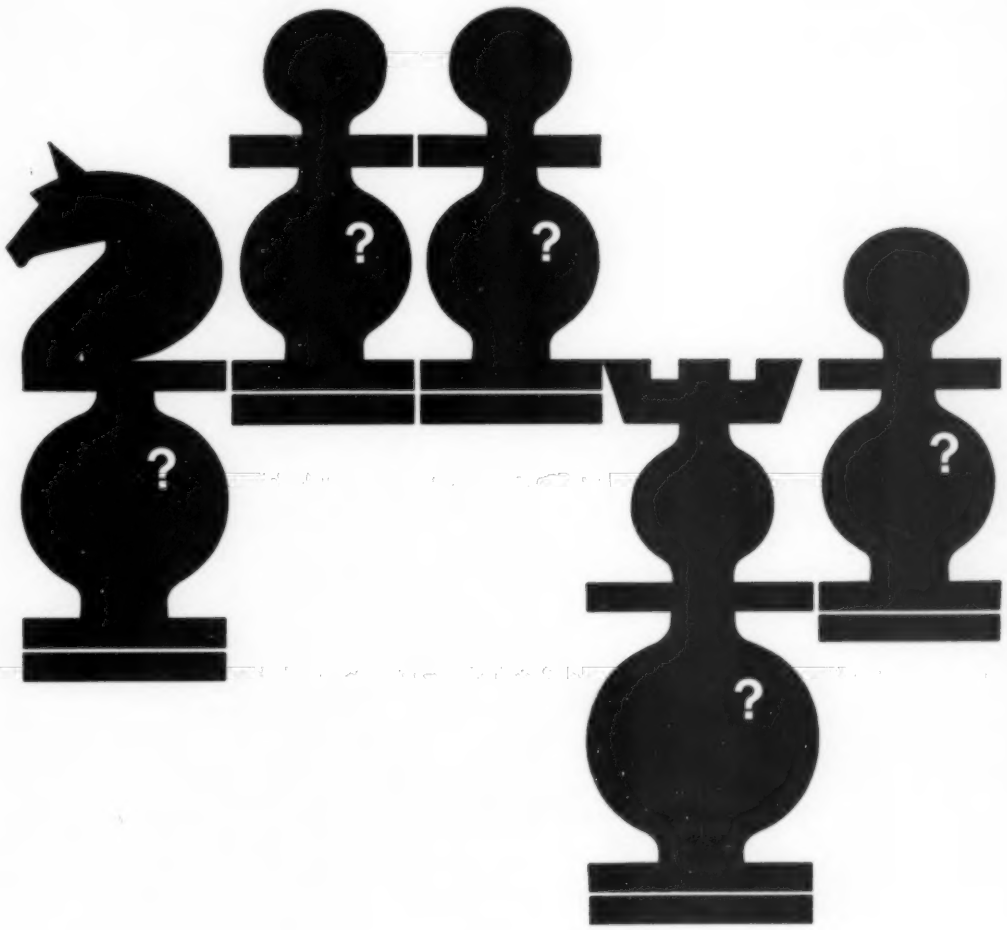

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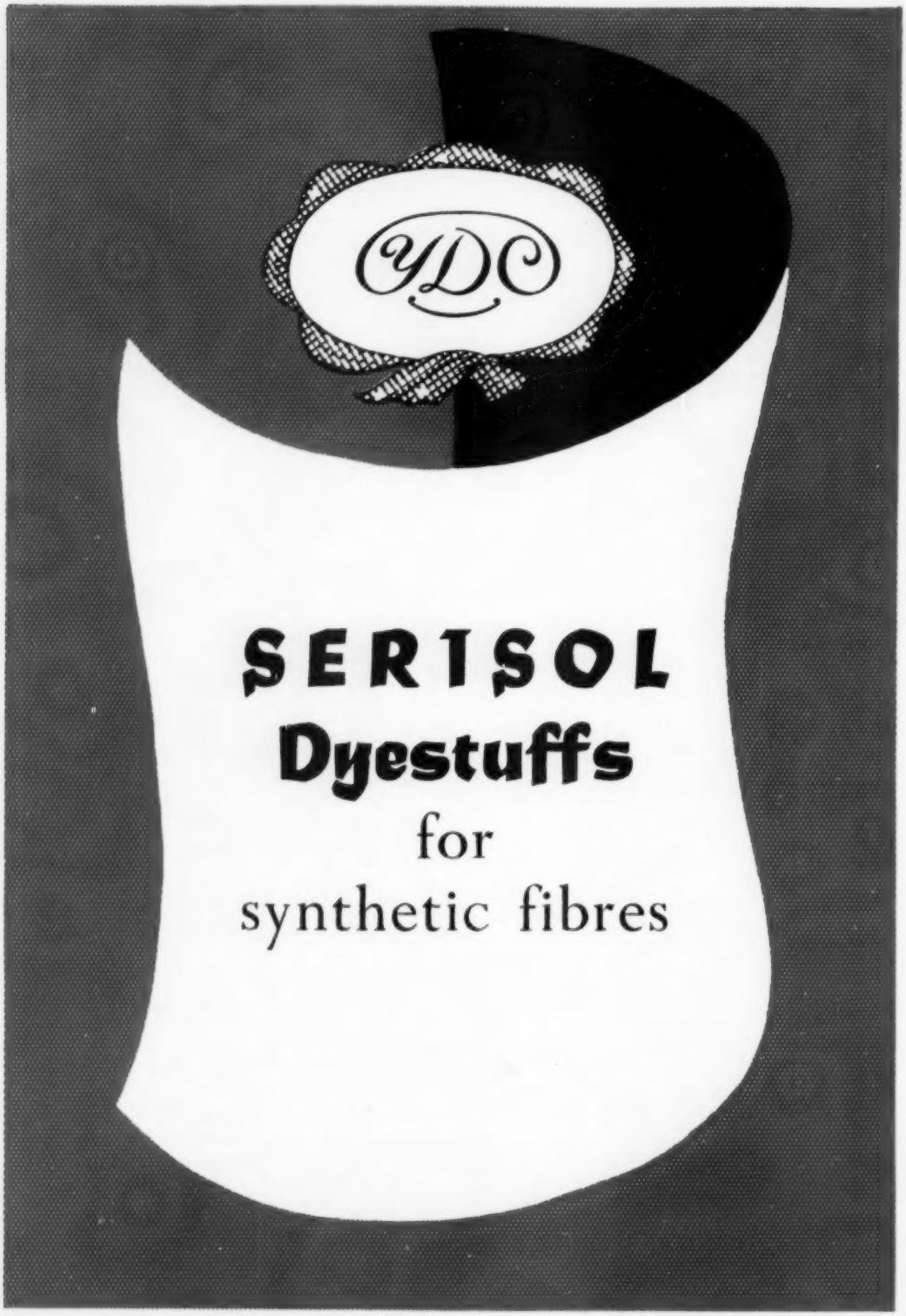

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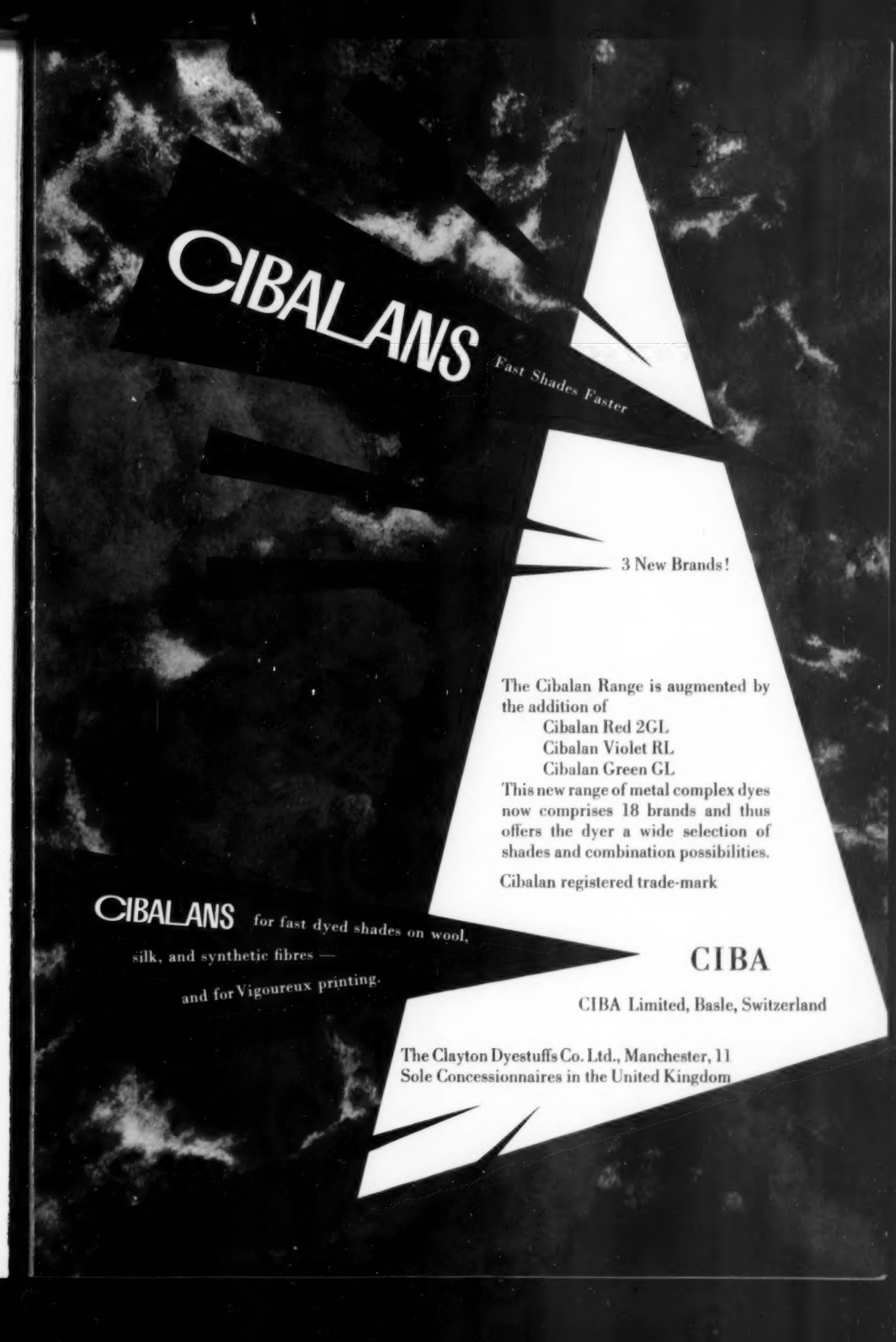
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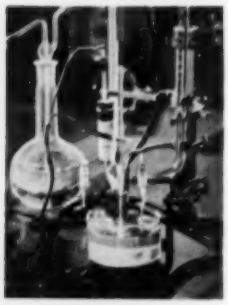

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does not occur in the absence of dispersing agent, it can be detected when the results are plotted as in Fig. 1–5. Several different solvents were tried

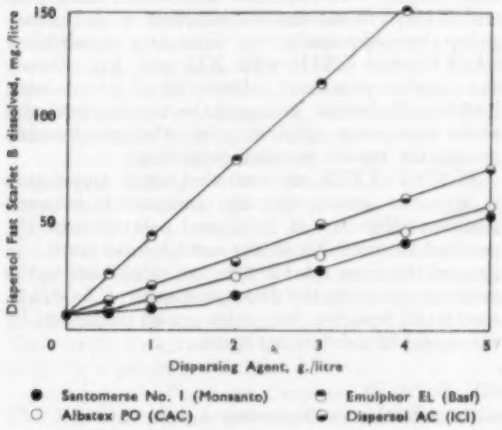

FIG. 1

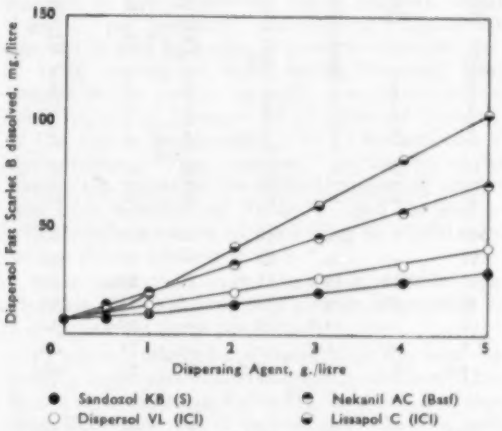

FIG. 2

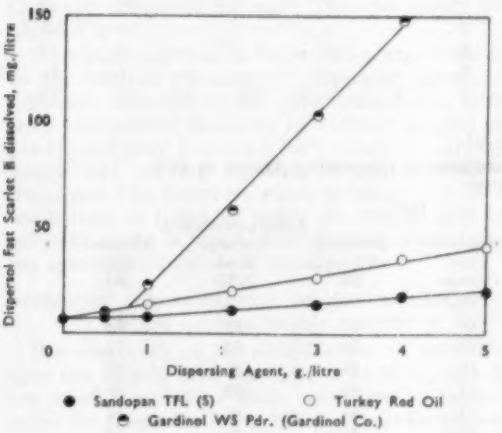

FIG. 3

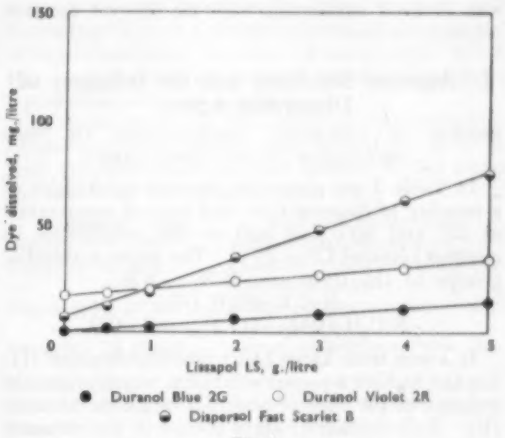

FIG. 4

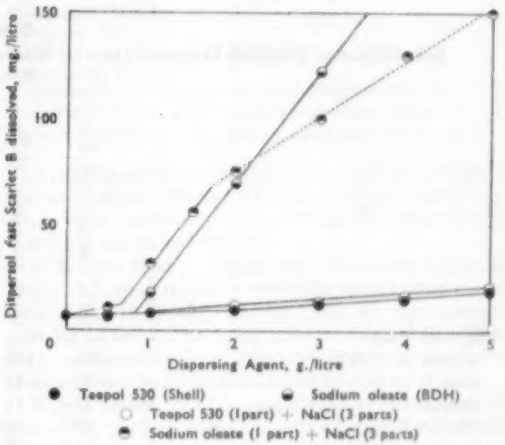

FIG. 5

with compound XXVI, but in each case the product was obtained in powder form, so no figures for solubility in solutions of dispersing agents are given for this dye.

Dyeings

Twofold 140/26 bright Celanese yarn, with 10 t.p.i. twist, was used. This was desized by Soxhlet extraction for 24 hr. with petroleum ether (40–60°C.), followed by drying, washing in running tap water for 24 hr., washing in distilled water, and drying. The desized yarn was stored in a humidity room at 65% R.H. and 22°C. One-gram hanks of this yarn were dyed in stainless-steel cages enclosed in Pyrex test-tubes fitted with a rubber bung. A vertical traverse was imparted to each cage via a stainless-steel wire passing through a narrow glass tube in the centre of the bung. This apparatus replaced the usual open tubes in the Marney dyeing machine. At the completion of dyeing a sample of the solution was removed for colorimetric analysis. The dyed yarn was rinsed, squeezed, dissolved in acetone, and the dye estimated colorimetrically. The total dye estimated from analysis of fibre and residual dyebath

was in good agreement with the known amount originally added.

I—Aqueous Solubility and the Influence of Dispersing Agents

EFFECT OF CHEMICAL CONSTITUTION ON THE SOLUBILITY OF DISPERSE DYES

In Table I are given the aqueous solubilities of a number of disperse dyes and related compounds at 25° and 80°C., as well as the solubilities in purified Lissapol LS at 25°C. The water-attracting groups in the dyes are –N:N–, $-NH_2$, $-N(C_2H_5)(C_2H_4OH)$, $-N(C_2H_4OH)_2$, $-O-CH_3$, and –OH.

It is seen from Table I that aminoazobenzene (II) has the highest aqueous solubility, which is greatly reduced in the case of 4-nitro-4′-aminoazobenzene (V). Substitution of alkyl groups in the primary amino group further reduces the solubility (VI–IX), but an increase of solubility results when the alkyl groups are replaced by hydroxyalkyl groups (X and XI). Introduction of a 2-methoxy or 2-nitro group increases the solubility, notably with XIX (cf. VIII, IX, and XI with XVII, XVIII, and XIX). With the introduction of a 2-chloro group there appears to be a slight drop in solubility (cf. XIII and XXIII with XII and X). Among the anthraquinonoid dyes those containing hydroxyalkylamino groups have the highest, and those containing alkyl- or aryl-substituted amino groups the lowest, aqueous solubility.

If XXV–XXIX are excluded, some correlation is apparent among the azo compounds between aqueous solubility at 25°C. and solubility in 1% purified Lissapol LS at the same temperature. In general the most soluble dyes are solubilised to the greatest extent by the dispersing agent. As will be seen later, however, the order is also influenced by the choice of solubilising agent.

TABLE II

Solubilities of Purified Disperse Dyes in Water and in Solutions of Dispersing Agents at 80°C.
(mg./litre)

Dye	Water	0·1% Lissapol LS (ICI)	0·1% Lissapol C (ICI)	0·1% Dispersol VL (ICI)	0·1% Dispersol AC (ICI)	0·1% Sodium Oleate (BDH)	0·1% Sandozol KB (S)	0·1% Sandopan TFL (S)	0·1% Emulphor EL (Basf)	0·5% Emulphor EL (Basf)
Dispersol Fast										
Yellow A (XXX)	108	128	126	122	—	250	113	—	220	—
Red R (XI)	18	25	21	24	—	25	21	—	29	80
Orange G (V)	9·5	11·5	14	13	15	11·5	11	10	29	99
Scarlet B (X)	7	19	19·5	13·5	21	18	10	8	44·5	186
Crimson B (XXIII)	5	9·5	13·5	12	—	11·5	5	—	38·5	155
Red A	1·2	3·5	6·5	3	—	5·5	—	—	14	58
Orange A (VII)	0·5	4	3·5	4·5	3	4	2·5	2	27	140
Duranol										
Violet 2R (XXXVI)	17	20	21	19·5	32	20	21	17	25	59
Red X3B (XXXVII)	11	15	14·5	13	21	13	12	10	18	53
Red 2B (XXXIII)	7·5	11	13	11·5	—	14	—	—	19	70
Orange G (XXXII)	6·5	9	12	8	—	13	—	—	15	39
Red G (XXXIV)	5·5	7	10	7	—	9	—	—	10·5	21
Brilliant Blue G (XXXVIII)...	2	2	3	2	—	—	2	—	4	13
Brilliant Yellow 6G (XLIII) ...	1·2	3	2·5	2	—	—	—	—	4·5	20
Blue 2G	<0·2	3	2·5	2	3	—	1·5	1·5	13	75

TABLE III

Solubilities of Purified Disperse Dyes in 0·5% Solutions of Dispersing Agents at 80°C.
(mg./litre)

	Dye					
	Azo			Anthraquinonoid		
Dispersing Agent	Dispersol Fast Scarlet B	Dispersol Fast Orange G	Dispersol Fast Orange A	Duranol Violet 2R	Duranol Red X3B	Duranol Blue 2G
Sodium oleate ...	240	60	46	57	49	40
Emulphor EL ...	186	99	140	59	53	75
Lissapol C	104	31	18	36	36	17
Dispersol AC ...	76	41	11	81	52	12·5
Lissapol LS ...	74	26	17	34	35	14
Dispersol VL ...	41	29	21·5	27·5	20	8

SOLUBILITY OF PURIFIED DISPERSE DYES IN 0·1% AND 0·5% SOLUTIONS OF DISPERSING AGENTS AT 80°C.

For this series of experiments a number of Dispersol (ICI) and Duranol (ICI) dyes were chosen, since Vickerstaff[10] has already provided a considerable amount of information regarding their dyeing properties. Dyes were rejected which were known or believed to contain more than one coloured component. Dispersol Yellow 3G (XXVII) was rejected on account of the slowness with which it reached saturation, Dispersol Fast Orange B because it could not be obtained in crystalline form, and Duranol Brilliant Blue CB (XLI) because it was unstable below pH 7. There remained 15 dyes for which solubility determinations were made with 0·1% solutions of dispersing agents. For the 0·5% solutions only 6 dyes were used, except in the case of Emulphor EL (Basf). The results are given in Tables II and III, together with the aqueous solubilities at 80°C.

Leaving out of account Dispersol Fast Yellow A (XXX), which has unusually high solubility, it is seen from Table II that, in a normal acetate rayon dyebath containing dispersing agent at 80°C., the amount of dye in solution varies between about 2 and 20 mg. per litre. That this is a significant amount is seen by taking a concrete example, viz. a 1·5% dyeing of commercial Dispersol Fast Scarlet B 150 containing 25% pure dye, with an addition of 1 g. Lissapol LS per litre of dyebath. If the liquor : goods ratio is 50 : 1 the amount of dye present is 75 mg. per litre. At the end of the dyeing the whole of the residual colouring matter will be in solution (cf. Table II), and the system will therefore consist of dyed fibre in equilibrium with a dilute solution of dye.

It is seen that even the least soluble dye, Duranol Blue 2G, is slightly soluble in presence of 1 g. dispersing agent per litre.

Previous workers have stated that the best dispersing agent varies from one dye to another. That this is so is shown in Table III, in which it is seen that Emulphor EL is particularly effective with Dispersol Fast Orange A (VII) and Duranol Blue 2G, sodium oleate with Dispersol Fast Scarlet B (X), and Dispersol AC with Duranol Violet 2R (XXXVI).

No conclusions can be drawn from this work as to the relative efficiency of dispersing agents of different chemical types. The compounds used were commercial products of varying degrees of purity, and they contained fatty chains of varying length and varying amounts of inorganic salts. Emulphor EL, however, which is stated [11] to be a condensate of 1 mol. of castor oil with 40 mol. of ethylene oxide, is a particularly effective solubilising agent for a number of disperse dyes.

EFFECT OF CONCENTRATION ON THE SOLUBILISING ACTION OF DISPERSING AGENTS

Previous work on the solubilisation of insoluble dyes has largely been carried out at 25°C., and it has been found that little solubilisation occurs below the concentration at which micelle formation occurs. At the critical micelle concentration (C.M.C.) a sharp break in the curve appears, and thereafter there is a steady increase in the amount of dye solubilised. Increase of temperature raises the C.M.C., whilst addition of neutral electrolyte, e.g. sodium chloride, lowers it.

In order to study the effect of concentration, solubility determinations were carried out at 80°C. with purified Dispersol Fast Scarlet B (X) using the following dispersing agents—

Dispersing Agent	Chemical Constitution
Albatex PO (CAC) ...	Sodium alkarylsulphonate
Dispersol AC (ICI) ...	Disodium methylenedinaphthalenesulphonate
Dispersol VL (ICI) ...	Fatty alcohol–ethylene oxide condensate
Emulphor EL (Basf) ...	Castor oil–ethylene oxide condensate
Gardinol WS Pdr. (Gardinol Co.) ...	Sodium lauryl sulphate
Lissapol C (ICI) ...	Sodium oleyl sulphate
Lissapol LS (ICI) ...	Sodium oleyl-*p*-anisididesulphonate
Nekanil AC (Basf)	
Sandopan TFL (S)	
Sandozol KB (S) ...	Sulphated oil
Santomerse No. 1 (Monsanto)	Sodium alkarylsulphonate
Teepol 530 (Shell) ...	Sodium *sec.*-alkyl sulphate
Turkey Red oil ...	Partly sulphated castor oil

The results are given in Fig. 1–3. Fig. 4 illustrates the solubilising effect of Lissapol LS on three disperse dyes, whilst Fig. 5 illustrates the effect on the C.M.C. of added electrolyte.

It is seen that in some cases the relationship is linear, whereas in other cases the curve consists of two straight lines, the gradient of the second portion of the curve being greater than that of the first. Absence of an inflexion does not indicate that no micelle formation takes place.

Fig. 5 shows that a considerable advantage is gained by adding common salt when using sodium oleate as dispersing agent. At a concentration of 1 g. of sodium oleate per litre, the amount of dye solubilised is almost doubled by adding 3 g. of sodium chloride per litre. At higher concentrations of soap salting out occurs, as indicated by the broken line in Fig. 5. With Teepol 530 (1 part) little improvement is obtained by adding salt (3 parts).

Table III shows that the order of efficiency indicated in Fig. 1–5 would have been somewhat different if another dye had been used, but it is believed that Fig. 1–5 give an approximate indication of the relative solubilising efficiency of the different commercial dispersing agents over the whole range of disperse dyes, although Tables II and III show that Emulphor EL is generally superior to sodium oleate.

It is probable that the shape of the curves in Fig. 1–5 is of general application, i.e. the increase in solubility for a 0·5% solution of dispersing agent is always equal to or greater than five times the increase in solubility produced by a 0·1% solution. Within the limits of experimental error, this view is supported by the figures in Tables II and III. Whether or not the curve shows an inflexion appears to depend to some extent on the dye, as well as on the dispersing agent, since a straight line

TABLE IV

Relation between Aqueous Solubility and (a) Rate of Dyeing and (b) Levelling Power on Acetate Rayon and Nylon

Dye	Aqueous Solubility at 80°C. (mg./litre)	Time of Half-dyeing on Acetate Rayon at 85°C.[10] (min.)	Levelling on Nylon at 85°C.[10]	Levelling on Acetate Rayon at 80°C.[13]
Dispersol Fast Yellow A ...	108	0·75	4	4
Dispersol Yellow 3G	>20	1·0	4	–
Dispersol Fast Red R	18	3·3	4	4
Duranol Violet 2R	17	3·0	4	4–5
Duranol Red X3B	11	4·8	4	4–5
Dispersol Fast Orange G ...	9·5	0·8	4	3
Duranol Red 2B	7·5	2·4	4	4
Dispersol Fast Scarlet B ...	7	4·0	3	2–3
Duranol Orange G	6·5	3·6	4	3
Duranol Red G	5·5	—	3	–
Dispersol Fast Crimson B ...	5	16·5	2	3
Duranol Brilliant Blue G ...	2	16·5	3	–
Duranol Brilliant Yellow 6G ...	1·2	4·7	2	–
Dispersol Fast Red A	1·2	—	2	–
Dispersol Fast Orange A ...	0·5	14·0	2	1–2
Dispersol Fast Orange B ...	0·2	19·0	1	1–2
Duranol Blue 2G	<0·2	28·5	1	–

relationship was obtained with Duranol Violet 2R (XXXVI) and Lissapol C, whereas an inflexion occurs with Dispersol Fast Scarlet B (X) (Fig. 2), which is solubilised to a much greater extent (cf. Fig. 4).

II—The Relation between Aqueous Solubility and Dyeing Properties

EFFECT OF AQUEOUS SOLUBILITY ON RATE OF DYEING

It is seen from columns 2 and 3 of Table IV that there is no correlation between aqueous solubility and the figures for rate of dyeing given by Vickerstaff [10]. This is to be expected, since the governing factor in rate of dyeing is normally the rate of diffusion in the fibre, which is unlikely to bear any close relationship to aqueous solubility. However, with the exception of Duranol Brilliant Yellow 6G (XLIII), it is found that the least soluble dyes, viz. Dispersol Fast Oranges A (VII) and B, Dispersol Fast Red A, Duranol Brilliant Blue G (XXXVIII) and Duranol Blue 2G, all have high times of half-dyeing. If dyeing takes place from a saturated solution, very low solubility might act as a bottleneck. It seems probable that very low aqueous solubility results in slow dyeing, but a low rate of dyeing does not necessarily imply low aqueous solubility (cf. Dispersol Fast Crimson B (XXIII)).

In Vickerstaff's table [10] Dispersol Fast Orange G (V) is seen to be the most rapid-dyeing disperse dye on acetate rayon and the second most rapid on nylon, which suggest that, as regards rate of dyeing, no advantage is to be gained by increasing the aqueous solubility at 80°C. beyond 10 mg. per litre.

EFFECT OF AQUEOUS SOLUBILITY ON LEVELLING

In Table IV aqueous solubilities at 80°C. are compared with (*a*) figures for levelling on nylon at 85°C. obtained by Vickerstaff and (*b*) figures for levelling on acetate rayon at 80°C. given by Whittaker and Wilcock [12]. In Vickerstaff's tests a dyed hank of nylon was treated with an undyed hank in a blank dyebath at 85°C. for 2 hr. Since the amount of Lissapol LS used was small (0·2 g. per litre), its effect on the solubility of the dyes can be ignored. Whittaker and Wilcock's levelling tests were carried out on acetate rayon yarn at 80°C. for 4 hr. and no dispersing agent was added.

TABLE V

Percentage of Original Dye remaining in Bath after Dyeing at 80°C. for 4 hr. in 0·5% Solutions of Dispersing Agents

	Dye					
	Azo			Anthraquinonoid		
Dispersing Agent	1% Dispersol Fast Scarlet B 150	0·7% Dispersol Fast Orange G 300	2% Dispersol Fast Orange A 150	0·8% Duranol Violet 2R 300	1·7% Duranol Red X3B 300	2% Duranol Blue 2G 300
Sodium oleate ...	59	29	29	37	27·5	40
Emulphor EL ...	47	44	60	40	32·5	53
Lissapol C	37	20	19	30	24	24
Dispersol AC ...	39	26	15	37	31	18
Lissapol LS ...	26	13	16	28	22·5	20
Dispersol VL ...	19	16	19	24	17·5	10

The good correlation shown in columns 2, 4, and 5 of Table IV leaves little doubt that the levelling power of a disperse dye on acetate rayon or nylon is largely governed by its aqueous solubility.

EFFECT OF SOLUBILISATION ON EXHAUSTION OF DYEBATH

Conditioned acetate rayon yarn (1 g.) was dyed at 80°C. for 4 hr., using the dyes listed in Table III, the amounts of dye being adjusted according to the percentage purity of the commercial dyes, so that approximately equal weights were present. The volume of dye liquor was 80 ml. and each dye was dyed in presence of 5 g. of (*a*) sodium oleate, (*b*) Emulphor EL, (*c*) Lissapol C, (*d*) Dispersol AC, (*e*) Lissapol LS, and (*f*) Dispersol VL per litre. The dyed yarn was rinsed, squeezed, and dissolved in acetone, the amount of dye present then being estimated colorimetrically.

The results obtained are given in Table V. If the vertical columns in Table V are compared with those in Table III it is seen that, apart from two results with Dispersol AC, the order is the same. Since Dispersol AC is not a fatty chain compound like the others, and is not in fact used as a dyebath addition, but as a ball-milling assistant, it is concluded that the restraining action of the dispersing agents used when dyeing acetate rayon with disperse dyes is proportional to their solubilising power, which, as has been shown earlier, varies with individual dyes.

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The Effect of Dyeing on the Sorption of Water Vapour by Wool*

P. LAROSE

The reduction in the sorptive capacity of wool for water vapour due to acid treatment or dyeing of the wool is discussed and previous results are reviewed. Preliminary experiments carried out with a view to showing a relation between the reduction in the amount of water sorbed and the amount of dye in the wool are reported. The results of these experiments point to an equivalence between the dye in the wool and the reduction in regain of the dyed wool as compared with undyed wool.

INTRODUCTION

The sorption of water by wool is known to be affected by dyeing and other finishing processes, but there is little evidence of a quantitative nature in the literature to show to what extent the regain of wool varies according to the pretreatment given to the fibre. Shorter, Hirst, and Hall [1] studied the changes in moisture-absorbing capacity produced by dyeing and other processes and noted that the hygroscopic capacity of cloth dyed with acid dyes or treated with acids was markedly reduced, but since the dye content of the wool was unknown, no quantitative relation between dye and regain can be drawn from their results. However, it is possible to use some of their results obtained with sulphuric-acid-treated wool to deduce such a relation, and this will be discussed later. Gillam [2] also studied the effect of various treatments on the regain of wool; however, his results do not lend themselves to theoretical treatment. Moreover, some of the results reported are contradictory. His Table 13, for example, indicates that the regain is lower as the result of various dyeing procedures, and indeed there is a rough correlation between the amount of acid and dye used and the reduction in regain, as the present Table I, a rearrangement of some of Gillam's results, shows. However, another set of dyeings, reported in his Table 15, shows, on the contrary, an increased regain for the dyed tops as compared with the regain of white wool.

A large number of fabrics examined in our laboratory during the Second World War also showed a wide variation in regain when conditioned at 65% R.H. and 70°F. Drab serges were found to have moisture regains varying from 12·5 to 14·5%, drab friezes 12·3–15·2%, blue serges 12·2–15·0%, and drab meltons 12·4–14·7%. These variations in all-wool materials undoubtedly reflect the effect of various dyeing procedures and finishing treatments.

TABLE I

Effect of Dyeing on the Regain of Wool at 51% R.H. and 90°F.

(Gillam's Data [2] rearranged)

Wool Sample	Amount of Dye used (%)	Amount of Acid used (%)— Acetic	Sulphuric	Residual Acid in Wool (as % H_2SO_4)	Regain (%)
White ...	—	—	—	—	11·56
Light blue	0·06	0·25	0·25	0·26	10·26
Green ...	0·28	0·50	0·50	0·25	10·12
Mauve ...	0·24	0·50	0·50	0·53	9·91
Dark blue	2·30	1·00	1·00	0·80	9·63
Orange ...	0·58	0·50	1·00	0·56	9·46
Red ...	4·20	0·50	1·00	—	9·19

Das and Speakman [3] mentioned the effect of sulphuric acid in wool in reducing the absorptive

*Issued as N.R.C. No. 3184.

capacity of the wool for water, and they give results of earlier experiments which show the reduction in regain for wool containing two different amounts of sulphuric acid.

While carrying on an investigation on the sorption of Orange II by wool, we noticed that the weight of our conditioned dyed samples varied appreciably with the conditions of dyeing, and it was decided to carry out moisture absorption tests on the dyed wool with a view to obtaining some relation, if possible, between the amount of dye sorbed and the regain of the dyed wool. This communication gives the results of preliminary experiments carried out in this direction.

EXPERIMENTAL

Two different experiments were carried out. In the first, three samples of wool yarn, commercially scoured but not otherwise treated, were dyed with different quantities of Orange II by boiling for one hour in the dye solution containing 2·2% sulphuric acid (based on the weight of wool) and using a liquor ratio of 50 : 1. After dyeing, the wool was rinsed with three portions of 25 ml. of distilled water to remove adhering dye solution. The wool was then allowed to dry at room temperature, and the drying completed at 105°C. for one hour. Two other wool samples were treated in the same way except that the dye was omitted from the acid solution, and a sixth sample was boiled in water only. After drying, these samples were conditioned in an atmosphere of 65±1·0% R.H. and 70±0·5°F. and weighed on three successive days, the first weighing being carried out 24 hr after the introduction of the samples into the conditioning room. The amount of dye and acid sorbed by the wool was calculated from the change in concentration of the bath before and after dyeing. The figures obtained in this way are somewhat larger than the true amount sorbed, since the rinsing with water after dyeing removes some of the acid and dye. However, experience has shown that the amount of dye removed is small under the conditions employed, although there is a greater degree of uncertainty regarding the sulphuric acid remaining in the wool.

In the second experiment an attempt was made to determine the effect of the dye only by soaking the wool in a large volume of distilled water for 15 hr. in order to remove most of the acid after dyeing. These samples had been dyed in the presence of oxalic acid, which is probably more readily rinsed out than sulphuric acid. The amount of dye remaining on the fibre was known more accurately than in the first experiment, since it was determined directly by dissolving the wool in a minimum quantity of dilute alkali and measuring the amount of dye in the solution colorimetrically. Standard dye solutions of the same alkalinity were used for comparison.

Sorption isotherms were determined on these samples by weighing the samples directly in an evacuated sorption apparatus in which water vapour could be introduced. The samples were suspended on McBain quartz spirals, whose lengths were read by means of a cathetometer, which was also used to read a mercury manometer indicating the equilibrium vapour pressure. The samples were initially dried over phosphorus pentoxide in the sorption apparatus after evacuation. The sorption was carried out at room temperature, and although no attempt was made to maintain the temperature constant, a thermally lagged air chamber around the sorption tubes kept the temperature variation between readings to within a fraction of a degree. This was not serious, since in all cases the water sorption of a white untreated sample was measured at the same time. Samples containing four different amounts of dye were tested in this way.

RESULTS

In Table II are given the results of the first experiment with the wool conditioned at 65% R.H. It should be noted that the white wool which was simply boiled showed a regain which was identical within experimental error to that regularly found for untreated samples. The presence of acid in the wool evidently exerts a marked effect in reducing the sorption of water vapour, and this reduction is enhanced by the dye, although the influence of the dye is not significant when the dye content is low.

The results of the second experiment are given in the form of sorption isotherms in Fig. 1. The

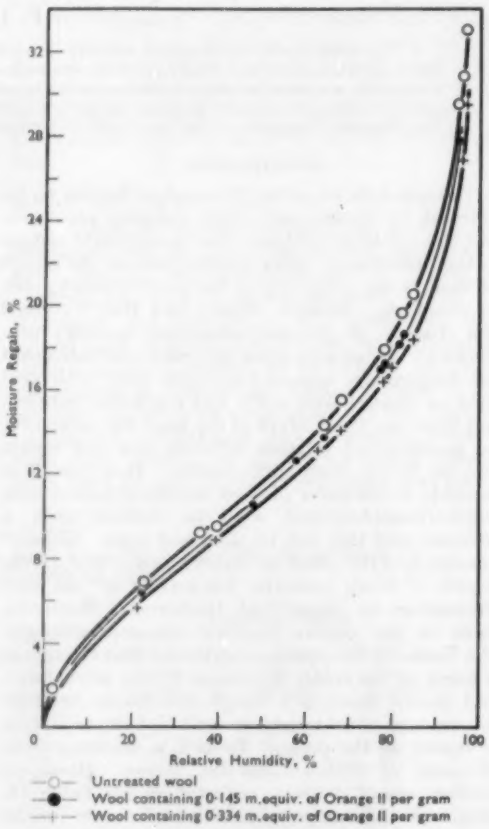

FIG. 1—Isotherms for Sorption of Water Vapour by Wool.

TABLE II

Effect of Acid and Dye on the Regain of Wool at 65% R.H. and 70°F.

Sample	Treatment	Regain*
1	Boiled with dist. water	15·65
2	Boiled in 0·0084 N-H_2SO_4 Final pH 2·94 Acid in wool 0·45 m.equiv/g. ...	14·70
3	As Sample 2	14·85
4	Boiled with dye and H_2SO_4 solution. Dye in wool 0·041 m.equiv./g. ...	14·70
5	As Sample 4 but with dye content 0·33 m.equiv./g.	14·27
6	As Sample 4 but with dye content 0·48 m.equiv./g.	14·13

* The regain is calculated on the dry wool weight corrected for the estimated amount of acid and dye in the wool.

moisture regain was calculated on the weight of wool substance, as for Table II, by correcting the sample weight for the amount of dye in the wool. The results of two only of four samples tested are shown in Fig. 1 in order not to obscure the curves drawn. One of the samples omitted had 0·47 m.equiv. of dye per gram of wool and showed a decrease in regain, as compared with the undyed sample, somewhat larger than that obtained for the sample with 0·33 m.equiv. of dye. The other sample not shown in Fig. 1 had 0·60 m.equiv. of dye per gram of wool. This sample yielded anomalous results in that its regain was practically the same as that of the sample containing 0·33 m.equiv. of dye. One interesting feature of the sorption results is that the difference between the regain of the dyed wool and that of the undyed wool expressed as a percentage of the latter is almost constant over most of the relative humidity range investigated. The standard deviation in Table III shows the extent of the variation encountered in measuring this difference in regain at various relative humidities.

TABLE III

Decrease in Regain of Dyed Samples

(Average for entire sorption curve)

Dye Content (m.equiv./g.)	Decrease (%) in Regain based on Regain of Undyed Wool	α
0·15	3·9	0·8
0·33	10·8	1·1
0·47	13·7	1·0
0·60	10·0	1·5

α = Standard deviation of the results given in the second column calculated from the actual experimental differences observed.

At low relative humidities (<6%) the decrease in regain had a tendency to be greater than the mean figures reported in Table III. Desorption results were obtained with the sample containing 0·47 m.equiv. of dye and these gave a mean regain difference very close (13·0%) to that of the sorptive process, when compared with the desorption regain of untreated wool.

DISCUSSION

If the sorption of acids, including acid dyes, by wool involves the neutralisation of polar groups, as is generally believed, and if the polar groups in the wool are also responsible for its sorption of water vapour, presumably by hydrogen bonding, a view widely accepted, then it is to be expected that wool which has sorbed a certain amount of acid will have its capacity for absorbing water reduced to the extent that its polar groups have been rendered ineffective by the sorbed acid. The results of our experiments and those mentioned in the introduction apparently confirm this.

The results of Shorter, Hirst, and Hall[1] are generally not sufficiently complete to allow ready calculation of a relation between acid or dye content and the regain, but such a calculation is possible for some of the samples on which determinations of sulphuric acid had been made. Table IV gives some of these results arranged to show this relation. The approximate constancy of the factor K indicates that the reduction in regain is roughly proportional to the acid content of the wool. The relative humidity at which these regains were observed is not available in the work of Shorter, Hirst, and Hall, but judging from the regain given for the untreated wool it must have been close to 70%.

TABLE IV

Relation between Sulphuric Acid Content and Regain of Wool

(Tested by Shorter, Hirst, and Hall[1])

H_2SO_4 (m.equiv./g.)	Regain	Reduction in Regain (m.mole./g.)	K
0·0	16·09	—	—
0·137	15·37	0·40	2·92
0·141	15·88	0·12	0·83
0·198	15·32	0·43	2·16
0·288	15·19	0·50	1·74
0·290	15·17	0·51	1·71
0·306	15·18	0·51	1·65
0·306	15·07	0·57	1·85
0·308	15·27	0·46	1·48
0·310	15·49	0·33	1·08
0·331	15·02	0·60	1·80
0·337	15·22	0·48	1·43
0·359	14·88	0·67	1·87
0·374	15·00	0·61	1·62
0·461	14·70	0·77	1·67
		Mean	1·70

K = Ratio of reduction in regain, expressed as m.mole of water per gram of wool, to H_2SO_4 content, in m.equiv. per gram of wool.

A similar comparison between the isotherms reported by Das and Speakman[3] yields very much the same result. At 70% R.H. the regain of untreated wool is 16·2% as closely as could be read from their curves, while the regain of wool containing 0·42 m.equiv. of acid per gram is 15·0% and that containing 1·00 m.equiv. of acid is 13·5%.

The corresponding reductions of 1·2 and 2·7 in regain give values of 1·6 and 1·5 respectively for K, figures of the same order as the values given in Table IV. The significance of these values will be discussed later.

Referring now to our results in Table II, it is not possible to obtain for samples 2 and 3 an exact relation between the reduction in regain and the acid content, since the latter is not known with any degree of certainty. The figures obtained with the dyed wool, however, are more useful.

Reductions of 1·38% in regain for sample 5 and of 1·52% for sample 6 give value of K of 2·32 and 1·76 respectively. These are for 65% R.H., which would be expected to yield values about 8% lower

than for 70% R.H. On the other hand, these values of K are somewhat high, since a small amount of sulphuric acid remaining in the wool was not taken into consideration.

Table V gives the reduction in regain at 70% and the corresponding values of K for the four samples of dyed wool tested in the second experiment and listed in Table III.

Except for the last one, the values of K are larger than those found for sulphuric acid treated wools but close to the value of 2·3 given by sample 5 in the first experiment. The mean of the first three values of K in Table V is 2·5.

TABLE V

Reduction in Regain for Dyed Samples at 70% R.H.

Dye Content (m.equiv./g.)	Reduction in Regain at 70% R.H.	K
0·15	0·61	2·3
0·33	0·70	2·8
0·47	2·15	2·5
0·60	1·57	1·4

These results are probably best explained by referring to the work of Bull [5], who has measured the adsorption of water vapour by a number of proteins and analysed the results in the light of the Brunauer, Emmett, and Teller (B.E.T.) theory. Bull found that with wool his data indicated the formation of a monolayer when the regain was 6·58%. He also estimated another value, a_2, given on the adsorption isotherm by the point at which the isotherm departs from linearity, which for wool was 13·6% regain. This was interpreted as the point at which the water sorbed formed a double layer. The first point occurs at 21% R.H. and the other at 61% R.H. according to the data of Bull at 25°C. These figures are in very good agreement with the isotherm for untreated wool shown in Fig. 1.

By making use of the mean difference in regain given in Table III for the four samples of dyed wool tested in the second experiment, the difference in regain to be expected at 21% R.H. may be calculated. The results are given in Table VI, which also includes the change in regain to be expected were the dye sorbed to reduce the regain by an equivalent amount. The agreement between the figures in the second column and those in the third column is quite good, with the exception of the sample containing 0·60 m.equiv. of dye, if one considers the possible errors in the various quantities involved in the calculation.

If a monolayer is formed at 21% R.H. and a double layer at 61% R.H., as the data of Bull seem to indicate, then at 70% R.H. somewhat more than two layers of water may be expected to be sorbed on the active sites. Actually the ratio of the regain at 70% R.H. to that at 21% is 2·4 for untreated wool. If one supposes that each site occupied by acid or dye is inaccessible to water, then each equivalent of the acid or dye sorbed should reduce the regain at 70% R.H. by 2·4 moles of water.

The closeness of this figure to the value of 2·6 for the mean of the first three results in Table V together with the results of Table III which indicate that a similar relation holds at other humidities, lend strong support for the view that the acid or dye molecules occupy sites normally available for the sorption of water.

There is no apparent reason for the low value of K for the wool containing 0·60 m.equiv. of dye. One possible explanation may be that the higher concentration of dye solution required to give this adsorption of dye caused a more pronounced decomposition of the wool and thereby introduced additional hydrophilic groups.

An alternative way of analysing the results is to apply the B.E.T. equation to the sorption data and determine directly the regain corresponding to the formation of a monolayer. The reduction in regain obtained in this way is given in the fourth column of Table VI. Smith [6] has proposed a different method for calculating the amount of vapour sorbed when a monolayer is formed. Although his method is based on different assumptions regarding the condensed water from those of the B.E.T. theory, the amount of bound water which he calculated for a number of high polymers was in good agreement with that given by the B.E.T. method. The Smith method when applied to our results gave the differences in regain listed in the fifth column of Table VI. The results in the last two columns should be in better agreement, and the discrepancy is no doubt due to a large experimental error in the calculations resulting from too few points defining that part of the sorption isotherm which is extrapolated to obtain the intercept in the B.E.T. plot. The figure of 1·09 in the last column for the sample with 0·604 m.equiv. of dye is rather surprising in view of the regain of this sample, which was found to be too high by all other considerations.

TABLE VI

Reduction in Regain when Wool has sorbed a Monolayer of Water Vapour (Bound Water)

Dye Content (m.equiv./g.)	Reduction in Regain calculated from— Dye Content	Table III	B.E.T.	Smith[6]
0·15	0·26	0·27	*	0·18
0·33	0·60	0·70	1·23	0·60
0·47	0·84	0·89	0·80	1·11
0·60	1·09	0·65	0·40	1·09

* It was impossible to draw a good straight line through any section of the graph in this case.

The data of Das and Speakman [3] on the effect of sulphuric acid can be used in the same way to compare the reduction in regain with the theoretical reduction based on the acid content. At 21% R.H. as closely as could be read on the graphs reported, the regain for the undyed wool is 6·4%, that for wool containing 0·42 m.equiv. of acid is 5·7%, and that for wool containing 1·00 m.equiv. of acid is 5·2%, thus giving differences in regain of 0·7 and 1·2% respectively, while the differences to be expected from the sulphuric acid content are 0·76 and 1·80%.

The results which we have briefly discussed strongly suggest that wool which has sorbed acid or dye as dye acid has its sorptive capacity for

water vapour reduced by an amount which is equivalent to the amount of acid sorbed. In other words, the polar groups responsible for the sorption of water have become ineffective to the extent to which they have been neutralised by the sorbed acid.

Whether this deduction is general or not can be shown only by further experiments with other acids or dyes and with wool containing larger amounts of these than those reported here*.

NATIONAL RESEARCH COUNCIL
OTTAWA
CANADA
(*Received 15th June 1953*)

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* In a recent private communication, J. B. Speakman and C. H. Nicholls have indicated that there is a difference in the behaviour of different acids in this respect.

Disulphide Bond Reactivity in Wool—Formation of Thiol Radicals on Exposure to Light

G. H. CRAWSHAW and J. B. SPEAKMAN

On exposure to diffuse light, stringently de-aerated solutions containing methacrylic acid and sulphuric acid undergo polymerisation in a few hours at 25°C. in presence of ethyl disulphide, cystine, or intact wool, but not in their absence. The disulphides (including wool) are ineffective in the dark, and it is concluded that polymerisation is initiated by the thiol radicals which are produced by homolytic fission of the disulphide bonds under the influence of light—

$$R\text{-}S\text{-}S\text{-}R \underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}} 2\ R\text{-}S\bullet.$$

Two methods of promoting preferential polymerisation of vinyl compounds inside animal fibres have been described in previous papers[1]. In the second of these methods, wool was impregnated with a dilute solution of ferrous ammonium sulphate and then treated with a mixture of hydrogen peroxide and monomer, polymerisation being initiated within the fibres by the hydroxyl radicals which are formed by the reaction between hydrogen peroxide and the ferrous ions. Since the polymerisation of vinyl compounds is initiated by the products of dissociation of water by X- or γ-rays, and since a simple method of iodinating the tyrosine side-chains of wool is now available[2], it seemed possible that wool containing iodine-131 might itself promote internal polymerisation of vinyl compounds. The following investigation was undertaken to examine this possibility; it led to the discovery that the disulphide bonds of wool undergo homolytic fission during exposure to light, polymerisation being initiated by the thiol radicals which are formed.

EXPERIMENTAL

(*a*) *Purification of Wool*

The exposed tips of staples of Lincoln wool were cut off and discarded, the remainder being purified by extraction with alcohol and ether in a Soxhlet apparatus, followed by washing in distilled water.

(*b*) *Iodination*

To a quantity (15 millicuries) of iodine-131 in the form of iodide ion (Atomic Energy Research Establishment) was added 0·1 N. potassium iodide (5·0 ml.), followed by excess of a saturated solution of potassium iodate in 1·0 N. sulphuric acid. The mixture was centrifuged to separate the iodine, which was washed free from salts with distilled water, after removing the supernatant liquid. A 0·72 N. solution of the iodine in absolute alcohol (1·5 ml.) was then prepared. It contained all the iodine-131 and was used to iodinate a sample (0·04 g.) of the wool. For reference purposes, a second sample of wool was treated with iodine-127 under similar conditions. In both cases the reaction was allowed to proceed for 72 hr. at 25°C., and the wool was then washed 20 times with absolute alcohol to remove excess iodine. The washed wool, which was still yellow, was freed from adsorbed iodine by immersion in sodium thiosulphate solution (0·1 N., 50 ml.) for 24 hr. at room temperature and was then completely white. Sodium thiosulphate and iodide were removed by washing the wool in three changes of distilled water (50 ml.) over a period of 48 hr. After this treatment, the only iodine remaining in the wool is that combined with the tyrosine side-chains, 96% of which are converted into 3:5-di-iodotyrosine[2].

(*c*) *Polymerisation Experiments*

(i) IODINATED WOOLS—The concentration of radicals produced by nuclear radiations is normally small, and previous experience[3] had indicated that extremely stringent de-aeration of the monomer solution and a time of approximately 8 weeks would be necessary to obtain a substantial amount of polymerisation with wool containing iodine-131 as the initiator. Accordingly, each sample of iodinated wool was treated as follows—

A solution (100 ml.) containing methacrylic acid (5·0 ml.) and sulphuric acid (10·0 ml., 1·041 N.) was prepared. The wool was added to 10 ml. of this solution in a 25-ml. flask fitted with a ground joint which was connected through a glass tap to a high-vacuum line. After the solution had been frozen with a paste of solid carbon dioxide and acetone, the flask was evacuated to 10^{-5} mm. by means of a mercury diffusion pump. The tap was then closed and the contents of the flask were allowed to melt so as to liberate dissolved air. Freezing and melting

were carried out three times in succession, and the flask was then placed in a thermostat at 25°C. After 18 hr. the solution in each flask had set to a gelatinous mass, showing that polymerisation takes place in absence of iodine-131 in a relatively short time.

(ii) CONTROL EXPERIMENTS—From first principles, it seemed possible that polymerisation might have been initiated in several ways. If, for example, a trace of thiosulphate were retained by the washed wool used in the preceding experiments, its decomposition by the acidic solution of monomer might give rise to free radicals. Alternatively, polymerisation might be initiated by groupings present in iodinated or untreated wool. In addition, exposure to the large surface area presented by the wool fibres might assist polymerisation of methacrylic acid under conditions of stringent de-aeration. Some of these possibilities were eliminated by the following experiments—

Into each of four 25-ml. flasks, which had been cleaned with chromic acid and washed thoroughly with distilled water, were introduced 10 ml. of the solution of monomer and sulphuric acid. In addition, the flasks contained, respectively, wool (0·05 g.) which had been treated with sodium thiosulphate solution (0·1 N.) for 24 hr. and washed as before; iodogorgoic acid (5 mg.); untreated wool (0·05 g.); and glass wool (0·05 g.). After de-aeration in the manner already described, each flask was transferred to a thermostat at 25°C. for 36 hr. At the end of this time the solutions in the flasks containing untreated and thiosulphate-treated wools were found to have set to a gel, whereas the contents of the flasks containing iodogorgoic acid and glass wool were mobile liquids.

(iii) AMINO ACIDS—As polymerisation is initiated by untreated wool, attention was next turned to the behaviour of particular groupings. Of those present, the disulphide bonds seemed most likely to give free radicals, and experiments were, therefore, carried out with cystine (5 mg.) and, for purposes of comparison, cysteine hydrochloride (5 mg.) and lysine (5 mg.), each in 10 ml. of the solution of monomer and sulphuric acid. After stringent de-aeration, the solutions were allowed to stand for 36 hr. at 25°C. The contents of the flask containing cystine were then found to have polymerised, whereas those of the other two flasks were still fluid.

(iv) INFLUENCE OF LIGHT—In order to discover whether photochemical or thermal fission of the disulphide bond is responsible for the formation of free radicals, further experiments were carried out as follows. Into each of six 25-ml. flasks were introduced 10 ml. of the solution of monomer and sulphuric acid. In addition, duplicate flasks contained wool (0·05 g.), cystine (5 mg.), and ethyl disulphide (5 mg.). The solutions were de-aerated as before, and one flask of each pair was quickly painted black. After 14 hr. at 25°C. polymerisation had taken place in each solution which had been exposed to diffuse light, but the painted flasks all contained mobile liquids. The paint was then removed from the three flasks, and exposure to diffuse light for 6 hr. resulted in the formation of a gel of polymer in each case.

DISCUSSION

There is much evidence to show that free thiol radicals R·S• can be formed by the dissociation of disulphides[4], and further support for this view is provided by the preceding experiments, in which the polymerisation of methacrylic acid was promoted by cystine and ethyl disulphide. Since cysteine, lysine, and iodogorgoic acid are without effect, there can be little doubt that the ability of intact wool to initiate polymerisation is due to the disulphide bonds it contains. At 25°C., however, cystine, ethyl disulphide, and wool are ineffective in absence of light, and it must be concluded that the free radicals which initiate polymerisation are formed by homolytic fission of the disulphide bonds under the influence of light—

$$R\text{–}S\text{–}S\text{–}R \xrightleftharpoons{h\nu} 2\ R\text{–}S\bullet$$

$$R\text{–}S\bullet + CH_2{=}C(CH_3)\text{–}COOH + CH_2{=}C(CH_3)\text{–}COOH + \cdots$$

$$\longrightarrow R\text{–}S\text{–}CH_2\text{–}C(CH_3)(COOH)\text{–}CH_2\text{–}C(CH_3)(COOH)\text{–}\cdots$$

$$\qquad\qquad\qquad

The Effect on Wool of Boiling in Aqueous Solutions
I—Solutions at pH 1·5–9 with and without Sodium Sulphate

R. V. PERYMAN

Wool of 64s quality, in the form of yarn and cloth, has been given boiling treatments of 3 hr. with 50 min. for raising to the boil to imitate prolonged commercial dyeing processes but without the addition of dye. The pH of the solutions has been controlled at selected pH values between 1·5 and 9 by the gradual addition of sulphuric acid or sodium carbonate during the boiling. The wool has subsequently been examined for modification by means of determinations of alkali solubility, soluble nitrogen, disulphide sulphur, total sulphur, breaking load air-dry and wetted with water, extension at break, abrasion resistance, and loss in weight. A smaller quantity of 56s Corriedale wool has been treated concurrently though subjected to fewer tests. The conclusions reached are— (1) the wools have suffered minimum modification when boiled at pH 3–3·5; (2) sodium sulphate, in concentrations up to 9·2 g./litre, has shown relatively little effect on the wool within the pH range 1·7–6·8, but above pH 6·8 the presence of sodium sulphate has caused alkali damage, which increases rapidly with increase of salt concentration and rise of pH; (3) a strong correlation has been found between disulphide content and wet breaking load for treatments having pH values above 4; a similar correlation has been found to apply to abrasion resistance after about 20% of the original disulphide sulphur has been broken down; (4) alkali solubility and soluble nitrogen have shown a strong correlation with abrasion resistance and to a lesser extent with wet strength for treatments having pH values below 2·5. The practical implications are discussed.

The chief industrial processes in which wool is treated at the boil may be classified into those concerned with (*a*) dyeing and (*b*) imparting permanent set. In the first category are the many processes of dyeing, chroming, and mothproofing, while in the second are crabbing, setting, and potting. This serves as a broad classification based on function, but in terms of changes produced in the wool distinctions between the processes cannot be so sharply drawn, because the pH value of some dye liquors is the same as that of liquors used for imparting permanent set. In a study of the effect of boiling aqueous solutions on wool especial account should therefore be taken of the wide variation in the conditions of commercial practice with regard to possible changes produced in the fibre. Numerous studies [1–6] have been published of the effect on wool of dyeing at the boil, but, with the exception of those of Lister [5] and Hannay *et al.* [6], alkaline dyeing conditions have generally been neglected. Two papers [7, 8], however, have been devoted to studies of the treatment at the boil of wool yarn and human hair, mainly in buffer solutions over a wide pH range and in the absence of dye, but unfortunately the amount and the nature of the electrolyte did not fully cover the conditions of commercial dyeing.

The assessment of changes in fibre properties produced by these or similar wet processes has been essayed by numerous workers, who have relied largely either on physical or on chemical methods. The physical methods used have included, in addition to the conventional measurements of breaking load and extension of yarn and cloth and the abrasion resistance of cloth, the measurement of the abrasion resistance of cloth whilst wet [9], the changes in work of extension of single fibres [8, 10], the setting power of single fibres [11, 12], and the power of supercontraction of single fibres [13, 14] and of yarn [15, 16]. The chemical methods used have been those of Pauly and Binz [17] with Rimington's modification [18], alkali solubility [19, 20], total sulphur [21, 22], thiol and disulphide sulphur [23, 24], and a number of dye absorption procedures of less general applicability. The multiplicity of the foregoing methods of test is itself evidence of the lack of a universal method for the measurement of damage in wool and that the methods of test must be chosen according to the type of damage in question. It is further to be noted in the work just reviewed that when numerous physical measurements have been carried out there has been a lack of chemical measurements, and *vice versa*.

With the foregoing observations in mind, the present investigation was designed to include a wider range of treatment and a more detailed physical and chemical examination of the wool than in any series of experiments hitherto published. Special attention has been given to properties of probable industrial importance which are also amenable to routine measurement in the laboratory.

EXPERIMENTAL

Selection and Preparation of Wool

As fine wools are more liable to show damage than coarse, wool of 64s quality was chosen for the experiments. A 160-lb. lot of 64s tops from Australian wool of good fibre uniformity, having a mean fibre length of 4·7 cm. and low apparent chemical damage, was processed into 2/14s and 2/15s yarn, the twist in each being 5·75×4 and 7·5×5 t.p.in. respectively and also into a 16-oz. plain-weave cloth with 37 ends and 34 picks of 2/16s yarn per inch (12×8 t.p.in.). After a mild scouring treatment, using Lissapol N and sodium chloride at 47°C. for the yarn, and soap and soda ash at 40°C. for the cloth, the residual fatty matter of the yarn and of the cloth (determined by ethyl ether extraction) was 0·18% and 0·13% respectively, and the subsequent alcohol extracts were 0·73% and 0·77% respectively. The ash content of the yarn was 0·41% after sulphation.

A much smaller quantity of knitted fabric and woven cloth, made from a carefully selected and scoured 56s New Zealand Corriedale wool, was also available for some of the experiments, thereby providing an indication of the comparative behaviour of a sound wool of coarser fibre. The cloth in this instance was a 2 × 2 twill with 68 ends and 67 picks per inch of 2/36s worsted yarn (16·5 × 18 t.p.in.).

Conditions of Treatment

Typical pH values of dye liquors range from 1·8 to 9·2 [25, 26], and dyeing recipes, when considered in relation to the liquor ratios used, indicate the presence of 0–10 g. of sodium sulphate per litre of liquor. The time of boiling may vary from about 45 min. to about 4 hr. Crabbing and setting liquors, though nominally of water only, are usually alkaline from residual alkali carried by the wool, whilst potting liquors are usually neutral to slightly acid according to the method of dyeing; less frequently, according to Marsh [27], the crabbing liquor contains soap or up to 1% sodium carbonate (on the weight of wool), and occasionally a 2% solution of borax is used, as recommended by Speakman [28].

For economy of effort, the liquor conditions chosen for the experiments (with one exception) were made to simulate the extreme conditions of commercial dyeing. Thus the time of boiling was fixed at 3 hr. with 50 min. for raising to the boil, the pH was held at values between 1·5 and 9·2, and the concentration of sodium sulphate was either 0 or 9·2 g./litre, with a few experiments at the intermediate concentration of 1·5 g./litre. In terms of practical dyeing, a sodium sulphate concentration of 9·2 g./litre corresponds to 20% Glauber's salt at the "short" liquor "length" of 11 : 1, and 1·5 g./litre corresponds to 15% Glauber's salt at the liquor "length" of 50 : 1.

The standard procedure was to wet out three 30-g. hanks of yarn together with a portion of Corriedale knitted fabric in warm distilled water under vacuum and pack so as to fill the small can of a Longclose stainless-steel laboratory dyeing machine, which was heated by gas, and the liquor circulated through the can by means of a motor-driven centrifugal pump. The liquor : wool ratio used was 67 : 1, which was the minimum practicable. Having made up the liquor containing the necessary additions to the required volume, it was raised to the boil in 50–55 min., boiled for 3 hr., and rinsed twice for 20 min. at 40–50°C. with filtered tap water softened with Calgon T. (Albright & Wilson). Up to this stage, the direction of flow of the liquor was reversed every 5 min., except that 10-min. intervals were used in rinsing. While bringing to the boil and while boiling, pH measurements of cooled samples of the liquor were made at 10-min. intervals with a Cambridge Instrument Co. glass-electrode pH-meter. When necessary, the pH value of the liquor was adjusted by means of small additions of dilute sulphuric acid or sodium carbonate. The samples taken for pH measurement were returned after measurement, and losses by evaporation were made good by the addition of boiling distilled water. After removal from the dyeing machine, the samples were neutralised to pH 4–5 overnight, either with a small excess of very dilute pyridine for the samples containing acid or with calculated amounts of very dilute sulphuric acid for neutral and alkaline samples. The neutralising process was followed by two further rinses in distilled water, hydroextraction, and air drying in the laboratory. The dry samples were subsequently kept in the humidity room at 20°C. and 65% R.H. (nominally).

The treatment of cloth followed a similar procedure, but with the following modifications—The weight taken was about 150 g., which was made up of two strips, one about 135 cm. × 27 cm. and weighing approx. 130 g., and the other, while making up the balance, also served for the determination of loss in weight. The strips were folded in lap form and boiled in a 13-litre stainless-steel bucket while loosely held between two perforated stainless-steel plates, separated by distance rods and so arranged as to keep the cloth completely immersed. A cover was fitted to the bucket during boiling, and additions of acid or alkali were made through a tube leading below the false bottom. As a further aid to the attainment of level treatment in the experiments in the alkaline range, the cloth was removed after boiling for 90 min., reintroduced end-for-end, and the boiling continued.

"Control" Treatment

It was anticipated that treatment of the yarn and the cloth under the experimental conditions used might give rise to changes in their characteristics which would be reflected in the measurements of strength, abrasion resistance, etc., but which would not be the result of chemical modification. Since the object of the work was to study changes in properties of the wool arising from chemical modification, it was necessary to eliminate as far as possible any effects which might arise purely from changes in physical characteristics of the yarn or cloth. With this object, the samples of both the yarn and the cloth required for the "control" measurements were subjected to special treatment with the object of reproducing the mechanical treatment to which the experimental samples had been subjected but under conditions of minimum chemical damage. For the yarn, three hanks were run at 40°C. in the dyeing machine at pH 3·1 for 1 hr., during which the circulation of the liquor was reversed 36 times to imitate the mechanical working given in the experiments. In other respects the subsequent treatment of the yarn was the same as given to the experimental samples.

The cloth "control" was produced by soaking in liquor at pH 3·3 at 40°C. for 90 min., stirring briefly at intervals of 10 min. The subsequent treatment of the cloth was the same as given to the experimental samples.

Analytical Methods

(1) ALKALI SOLUBILITY—The procedure of Harris and Smith [19], applied to duplicate 1-g. samples cut or pulled into ½-in. lengths of yarn, was used.

(2) ALKALI-SOLUBLE NITROGEN—Duplicate 1-g. samples of yarn from cloth or hank were cut into ½-in. lengths and immersed in 50 ml. of 0·5 N. sodium carbonate solution at 40°C. for 18 hr. After filtering, a 10-ml. aliquot of the filtrate was introduced into a micro-Kjeldahl flask, and the nitrogen determined by the procedure of Ma and Zuazaga [29]. The moisture content of the wool was

determined by drying a separate sample in an air oven at 105°C. Under these conditions about 0·5% of moisture is retained, and the term "dry weight" is used with this reservation throughout this paper.

(3) DISULPHIDE SULPHUR—Samples of wool (0·5 g.) were hydrolysed by boiling for 4 hr. under reflux with 20 ml. of 5 *N*. hydrochloric acid in a 100-ml. flask connected by means of a standard ground-glass joint with an open-ended tube of length about 150 cm. and 1 cm. bore, which served as an air condenser. After filtering, the hydrolysate was made up to 250 ml. with distilled water and the disulphide sulphur was determined using a 5-ml. aliquot by the method of Shinohara [30] using the phosphotungstic reagent of Folin and Marenzi [31]. The absorptiometric measurements were made with a Unicam spectrophotometer (Model SP 350 D.G.) set at 695 mμ. The small and practically constant amounts of thiol sulphur found in the hydrolysates were included in the results as disulphide sulphur. This procedure was taken as the simplest practical compromise in view of the claims that thiol sulphur can be produced [32] and destroyed [33] during the acid hydrolysis of proteins. Each recorded result is the mean of two or more determinations. Moisture was determined on a separate sample of wool.

(4) TOTAL SULPHUR—Samples of wool (0·5 g.), after steeping when necessary in a 2% sodium bicarbonate solution to remove extraneous sulphate, were digested according to the method of Jones [34] in a small Kjeldahl flask with 10 ml. of water, 6 ml. of nitric acid, 3 ml. of 60% perchloric acid, 3 ml. of 18% hydrochloric acid, and two or three glass beads. The sulphuric acid produced was weighed as barium sulphate. Each recorded result is the mean of two or more determinations. Moisture was determined on a separate sample of wool.

Physical Methods

(1) BREAKING LOAD AND ELONGATION OF YARN, SINGLE THREAD—A Goodbrand pendulum-type single-thread strength-testing machine was used, and samples of 2/15s yarn were broken at constant rate of traverse 12 in./min. in the humidity room using 20-in. test lengths for air-dry yarn and 16-in. lengths for wet yarn. Each recorded result is the mean of 36 measurements.

(2) BREAKING LOAD OF FIBRE BUNDLE, AIR-DRY AND WETTED WITH WATER—A Scott IP2 inclined-plane machine was used in the humidity room at constant rate of load 4 lb./min. with 0·5-cm. lengths of 2/14s yarn between the jaws. From separate determinations of the count of samples of the yarn on lengths ranging from 120 cm. to 160 cm., the breaking load measurements were corrected for count variation. Each recorded result is the mean of 36 measurements.

(3) BREAKING LOAD AND ELONGATION OF CLOTH, AIR-DRY AND WET—A Denison Model T42 machine was used at constant rate of load so as to break the patterns in approx. 1 min. Warpwise patterns, 9½ in. long and frayed to 2 in. wide from a cut width of 2½ in., were broken after clamping in the machine with 5 in. between the jaws. The number of ends in the warp of each pattern was subsequently counted, and the breaking load expressed in terms of a constant number of ends. Each recorded result is the mean of five measurements.

(4) ABRASION RESISTANCE—A solution to the problem of finding a method of measuring the abrasion resistance of fibres without the necessity of weaving them into a cloth has been found as the result of an experience in this laboratory when testing the abrasion resistance of uncut moquette fabric. It was found that the loops of the pile abrade in an exceptionally uniform manner on the Martindale machine [35], the end-point being sharp and easily recognised visually. Small quantities of yarn could not conveniently be woven into moquette, but an alternative method, in which loops of yarn were mounted between steel jaws lined with rubber pads, was adopted. By means of a specially designed frame 64 loops of 2/15s yarn were clamped in two rows each 0·5 in. long and were then abraded under a load of 300 g. against the standard crossbred cloth on the Martindale machine. When the count of the short lengths of yarn was found to vary from 2/15s worsted count, proportionate adjustment was made in the number of loops mounted. The abrasion resistance was taken as the number of cycles required to rub through the loops of the yarn. Each recorded result is the mean of four or more measurements.

(5) LOSS IN WEIGHT—Some preliminary trials showed that cloth, which had previously been extracted with ether and alcohol or acidified to pH 3 and extracted with ether, suffered abnormally high losses in weight when subsequently boiled. It was therefore decided to use cloth which had not been extracted and to apply corrections for changes in the amount of extractable matter. The following procedure was adopted—A pattern of the cloth weighing approx. 20 g. was dried to constant weight in a ventilated regain oven at 105°C., treated together with the rest of the cloth as already described, and its dry weight then redetermined, care having been taken to restore it to neutral reaction. After treatment, the matter extractable from the cloth by ethyl ether and subsequently by alcohol was determined. From these results and the amounts of the ether and alcohol extracts determined on a separate sample of the original cloth, an appropriate correction, ranging from 0·03 to 0·25% of the dry weight of the cloth, was applied to the loss in weight to allow for the small loss in the amount of extractable matter which took place during the boiling treatment.

RESULTS

The results of chemical tests on the yarn and cloth are given in Tables I and II and illustrated for disulphide sulphur and total sulphur contents in Fig. 1 and 2.

In comparing the results for yarn and cloth, it is necessary to remember that in boiling the latter less circulation of liquor could take place through the material, although the effective temperature was probably slightly higher. The uneven final colour of the cloth boiled in the alkaline buffer solutions indicated some unevenness of treatment.

TABLE I

Chemical Tests on Yarns

(Results in brackets are for Corriedale knitted fabric)

pH of Bath	Disulphide Sulphur (%) On Dry Wt.	Disulphide Sulphur (%) On Control Sample	Total Sulphur (%) On Dry Wt.	Total Sulphur (%) On Control Sample	Sulphur Ratio*	Alkali Solubility (%)	Soluble Nitrogen on Dry Wt. (%)
Control	2·95 (2·67)	100 (100)	3·52 (3·28)	100 (100)	84 (81)	13·4	0·162
BOILED FOR 3 HR., NO ADDED SODIUM SULPHATE							
1·45–1·5	2·96	100	—	—	—	66·5	1·04 (1·10)
2·14–2·2	2·91 (2·68)	98·5 (100)	—	—	—	35·0	0·422 (0·42)
2·8 –2·9	2·88	97·6	3·37	95·8	86	19·8	0·255
3·36–3·4	2·92 (2·64)	98·8 (98·9)	3·41	96·8	86	16·7	0·189 (0·19)
4·7	2·86 (2·51)	97·0 (94·0)	—	—	—	—	—
5·8 –6·1	2·63 (2·43)	89·0 (91·0)	3·41	96·8	77	12·9	0·201 (0·16)
6·0 –6·2	2·56 (2·47)	86·8 (92·3)	3·49	99·2	73	—	—
6·6 –6·9	2·49 (2·39)	84·4 (89·4)	—	—	—	—	—
6·9 –7·1	2·48 (2·33)	84·1 (87·4)	3·38	96·0	73	—	—
8·0 –8·3	2·36 (2·26)	80·0 (84·6)	3·30	93·7	72	—	—
8·7 –8·9	2·17 (2·21)	73·6 (82·7)	3·18	90·3	68	—	—
9·0 –9·2	2·08 (2·05)	70·5 (76·8)	3·18	90·3	65	—	—
BOILED FOR 3 HR., 1·5 g. SODIUM SULPHATE PER LITRE							
7·5 –7·9	2·30 (2·18)	78·0 (82·1)	3·40	96·6	68	—	—
8·0 –8·4	2·19 (2·09)	74·2 (78·5)	3·26	92·6	67	—	—
8·5 –8·9	1·85 (1·78)	62·7 (66·6)	3·01	85·5	62	—	—
BOILED FOR 3 HR., 9·2 g. SODIUM SULPHATE PER LITRE							
1·67–1·7	2·90	98·2	—	—	—	59·6	0·77
2·4 –2·42	2·92	98·8	3·43	97·4	85	26·2	0·352
2·84–2·9	2·94	99·6	—	—	—	19·9	0·235
3·8	2·94	99·6	3·47	98·6	85	14·5	0·182
4·5	2·83 (2·56)	96·0 (95·8)	3·42	97·2	83	—	—
5·8 –6·0	2·70	91·5	3·43	97·4	79	12·2	0·149
5·8 –6·1	2·65 (2·50)	89·8 (93·5)	3·48	98·8	76	—	—
7·0 –7·2	2·38 (2·33)	80·7 (87·4)	3·41	96·8	70	—	—
8·2 –8·1	1·82 (1·78)	61·7 (66·7)	3·03	86·0	60	—	—
8·4 –8·5	1·68 (1·65)	56·9 (61·8)	3·01	85·4	56	—	—
8·6 –8·7	1·37 (1·31)	46·4 (49·2)	2·84 (2·53)	80·6 (77·2)	48 (52)	—	—
BOILED FOR 30 MIN., 20 g. BORAX PER LITRE (Entered yarn at 90°C. and raised to boil in 5 min.)							
9·2 –9·16	1·36 (1·29)	46·1 (48·4)	2·78	79·0	49	—	—

* Sulphur ratio = $\frac{\text{Disulphide sulphur}}{\text{Total sulphur}} \times 100$

TABLE II

Chemical Tests on Cloths

(Results in brackets are for Corriedale woven cloth)

pH of Bath	Disulphide Sulphur (%) On Dry Wt.	Disulphide Sulphur (%) On Control Sample	Alkali Solubility (%)	Soluble Nitrogen on Dry Wt. (%)
Control	2·95 (2·67)	100 (100)	15·9 (15·5)	0·163
BOILED FOR 3 HR., 1·5 g. SODIUM SULPHATE PER LITRE				
1·94	2·90 (2·70)	98·3 (101)	54·7 (59·2)	0·585 (0·597)
2·6–2·7	2·90	98·3	26·3	0·263
3·0–3·1	2·94	99·6	—	—
3·1–3·2	2·91 (2·66)	98·6 (99·6)	21·6 (22·0)	0·214 (0·232)
4·4–4·5	2·84	96·2	—	—
5·0–5·2	2·79 (2·62)	94·6 (98·1)	15·7 (15·4)	0·163 (0·156)
5·9–6·0	2·65	89·8	—	—
BOILED FOR 3 HR., 0·0106 M. PHOSPHATE BUFFERS				
6·5–6·6	2·47	83·7	—	—
7·6–7·7	2·12 (2·05)	71·8 (76·8)	—	—
8·0–8·1	1·89	64·0	—	—
8·3–8·5	2·08 (1·79)	70·5 (67·1)	—	—
8·4–8·7	1·80 (1·57)	61·0 (58·8)	—	—
8·9–9·1	1·75	59·3	—	—

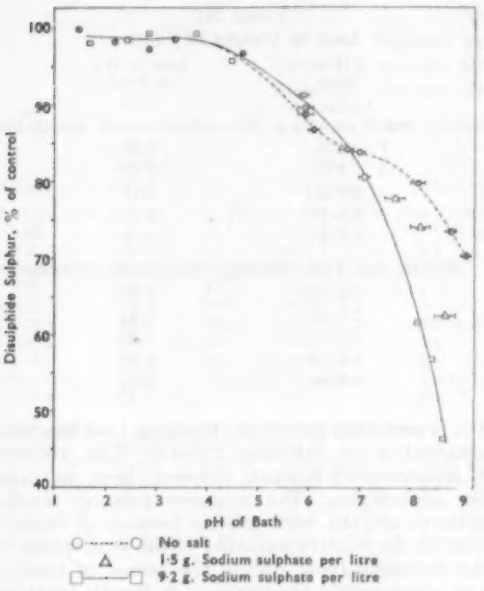

FIG. 1—Effect of pH of Boiling on Disulphide Sulphur Content of Yarn

As shown in Fig. 1, the presence of sodium sulphate has been found to have little effect in the acid range. Support for this view is evident in the fact that yarn and cloth boiled in the presence of 9·2 g. and 1·5 g. of sodium sulphate per litre respectively have similar disulphide sulphur and soluble nitrogen contents. The experiments in phosphate buffers, containing varying proportions of sodium and potassium phosphates, have served to extend the range of treatment of cloth in the alkaline range, but the results are not strictly comparable with those of the yarns treated in 1·5 g. of sodium sulphate per litre because of the different cations present.

Comparison of the results for disulphide sulphur and total sulphur with those obtained by Lindley and Phillips [24] on similar wool treated in acetic acid–acetate or boric acid–borax buffers shows that these authors found considerably lower amounts of disulphide and total sulphur at correspondingly alkaline pH values, but in the acid range they found slightly more disulphide sulphur. The differences between the results could, however, probably be explained in terms of vigour of boiling, anion affinity and ionic strengths of the solutions, and their use of benzene-extracted wool. The most significant difference between the present results and those of Lindley and Phillips is the evidence now shown of the important effect of salt in accelerating attack by alkali. An indication of this effect was observed by Steinhardt, Fugitt, and Harris [36] from their experiments at 0–50°C., but the present results emphasise the large increase when the temperature is raised to near 100°C. By reference to Fig. 1, it is seen that the presence of 9·2 g. sodium sulphate per litre has approximately doubled the extent of disulphide breakdown within the pH range 8–9 when compared with the effect in the absence of salt, while the effect of 1·5 g. sodium sulphate per litre has also been large, especially above pH 8·5. Further evidence of the extent of alkali attack has been found in the fact that the amount of sodium carbonate, based on the air-dry weight of wool, necessary to maintain a pH value of approx. 8·7 in liquors containing 0, 1·5, and 9·2 g. sodium sulphate per litre, has been 0·6, 1·2, and 2·3% respectively. As less than one-third of this alkali, as calculated from the results of Steinhardt and Harris [37], can be attributed to sorption by the wool, it would appear that the remainder has reacted with the disulphide sulphur.

The time of treatment, viz. 50 min. to the boil and 3 hr. boiling, has been constant with one exception. In this experiment, designed to imitate one method [28] of setting wool, the yarn was entered at 90°C. in a 2% borax solution, brought to the boil in 5 min., and boiled for 30 min. This treatment produced as large a fall in disulphide sulphur as the longer treatment at pH 8·6–8·7 in the presence of 9·2 g. sodium sulphate per litre. Apart from this one instance, the relationship of the duration of boiling to alkali attack has not been studied. It can be seen, however, from the results of Lindley and Phillips using buffer solutions, that above pH 8 the rate of attack on the disulphide sulphur is much greater in the first hour.

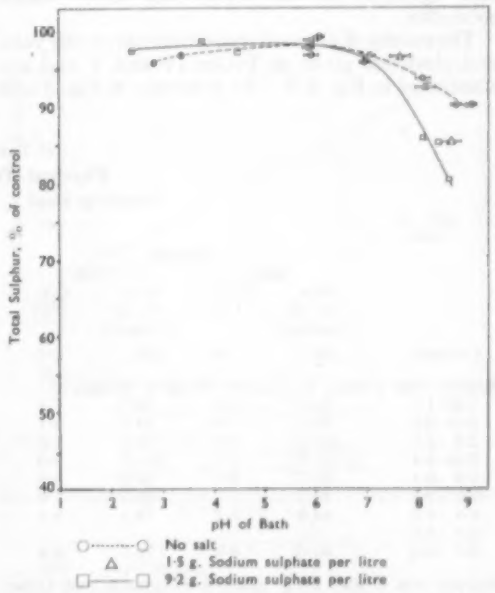

FIG. 2—Effect of pH of Boiling on Total Sulphur Content of Yarn

Fig. 2 shows that the total sulphur content of boiled wool, whilst showing a similar trend to that of disulphide sulphur, has changed to a much smaller extent. Thus total sulphur is relatively insensitive as a measure of alkali damage. In view of the loss of sulphur which has been found to occur from wool when boiled in alkaline solutions, the use of the ratio of the disulphide sulphur to total sulphur content, proposed by Schöberl [23] as a measure of damage, appears unsuitable as a measure of alkali damage.

The 56s Corriedale samples have shown a slightly higher resistance to alkali attack than the finer wool. This difference may probably have been due to the former having suffered more initial damage, as indicated by the lower disulphide content and sulphur ratio of the "control".

Evidence that acid damage has increased with increased acid content of the liquor has been found in the determinations of alkali solubility, in accord with the results of Ryberg [20], but the present results emphasise the steepness of the rise in alkali solubility as the pH value falls below 3. The results of soluble nitrogen determinations show good agreement between yarn and cloth and lend support to the alkali solubility results. In spite of increases in sorbed acid known to occur with increasing salt concentration [37], the presence of up to 9·2 g. sodium sulphate per litre has not increased the degree of acid damage, within the errors of measurement, indicated by either of these methods.

The losses in weight of wool incurred by boiling the cloth are given in Table III. While some difficulty has been found in obtaining reproducible results, it is clear that minimum loss of wool has occurred in the pH range 3–4 approx. Some lack of reproducibility is to be expected from observations [19, 38] that the degree of dispersion of the wool and agitation of the liquor can affect alkali solubility.

The results of physical measurements on the yarn and cloth are given in Tables IV and V and are illustrated in Fig. 3–9. By reference to Fig. 3 and 8 it is seen that maximum breaking load has been obtained in the pH range 2·8–4·0. The precision of measurement has not, however, been the same for all samples. The measurements on air-dry patterns are the least reliable because of fluctuations in the relative humidity of the atmosphere of the humidity room during the period of testing, and consequently the increases in bundle breaking load found above that of the "control" yarn are probably not significant. Most reliance is placed on the results for wet bundle breaking load. It should be remembered, however, in comparing the results of bundle breaking loads with other breaking loads, that the weight of wool in the bundle test

TABLE III

Loss in Weight of Cloth

pH of Bath	Loss in Wt. of Wool (%)
BOILED FOR 3 HR., 1·5 g. SODIUM SULPHATE PER LITRE	
2·2	1·23
2·8	0·73
3·0–3·1	0·71
3·8–4·3	0·75
4·3–5·0	1·08
BOILED FOR 3 HR., 0·0106 M. PHOSPHATE BUFFERS	
7·2–7·3	1·33
7·1–7·5	1·54
8·3–8·5	1·67
8·4–8·7	1·68
8·9–9·1	1·72

TABLE IV

Physical Tests on Yarns

pH of Bath	Breaking Load: Bundle Dry B.L. (% of Control)	Bundle Dry C.V. (%)	Bundle Wet B.L. (% of Control)	Bundle Wet C.V. (%)	Single Thread Wet B.L. (% of Control)	Single Thread Wet C.V. (%)	Elongation at Break, Single Thread Wet % of Control	Elongation at Break, Single Thread Wet C.V. (%)	Abrasion Resistance % of Control	Abrasion Resistance C.V. (%)
Control	100	7·6	100	9·1	100	5·6	100	3·8	100	7·6
BOILED FOR 3 HR. NO ADDED SODIUM SULPHATE										
1·45–1·5	94·2	5·9	68·7	7·8	60·8	5·2	93·8	3·5	—	—
2·14–2·2	96·5	7·8	84·2	8·1	76·0	6·1	99·0	3·3	66	4·4
2·8 –2·9	101·0	7·0	94·2	8·5	82·4	5·8	99·3	3·7	88	9·2
3·36–3·4	103·9	6·5	100·0	8·3	91·2	7·3	100·0	3·7	111	8·5
5·8 –6·1	95·7	6·7	88·2	8·8	74·4	6·3	93·8	4·2	119	16·8
6·9 –7·1	89·3	7·3	83·2	7·0	—	—	—	—	115	9·9
8·0 –8·3	84·3	8·7	79·8	8·4	—	—	—	—	106	7·4
8·7 –8·9	—	—	—	—	—	—	—	—	95	5·9
9·0 –9·2	81·6	6·9	79·3	8·8	—	—	—	—	94	9·9
BOILED FOR 3 HR., 1·5 g. SODIUM SULPHATE PER LITRE										
8·0 –8·4	—	—	—	—	—	—	—	—	95	5·6
8·5 –8·9	78·8	7·9	76·7	17·0	—	—	—	—	80	11·9
BOILED FOR 3 HR., 9·2 g. SODIUM SULPHATE PER LITRE										
1·67–1·7	89·5	6·3	72·6	8·0	68·8	6·7	98·0	3·2	55	4·2
2·4 –2·42	93·4	10·1	88·3	8·5	81·6	6·5	101·0	3·5	85	9·0
2·84–2·9	99·5	7·1	94·1	8·2	86·4	6·5	100·0	3·7	—	—
3·8	95·2	9·3	93·8	8·1	79·2	6·8	98·0	4·1	109	5·9
4·5	90·8	7·1	87·6	6·8	81·5	7·1	96·0	4·5	—	—
5·8 –6·1	86·5	7·0	82·2	8·9	75·0	10·0	92·6	8·5	107	10·9
7·0 –7·2	—	—	—	—	71·5	7·9	91·8	6·3	97	6·6
8·2 –8·1	78·3	8·2	70·5	7·2	59·0	7·8	90·2	6·1	77	2·4
8·4 –8·5	79·2	7·4	69·2	10·2	55·5	10·8	85·4	8·4	75	9·1
8·6 –8·7	76·8	8·7	63·4	9·2	53·5	11·7	87·2	8·4	69	6·8

B.L. = Breaking Load
C.V. = Coefficient of Variation of 36 measurements, except for abrasion resistance

TABLE V

Physical Tests on Cloths

(Results in brackets are for Corriedale woven cloth)

pH of Bath	Breaking Load, warpwise Not Neutralised Dry % of Control	Dry C.V. (%)	Wet % of Control	Wet C.V. (%)	Neutralised Dry % of Control	Dry C.V. (%)	Elongation at Break Not Neutralised Dry % of Control	Dry C.V. (%)	Wet % of Control	Wet C.V. (%)
Control	100	1·6	100 (100)	1·9 (2·7)	100	1·6	100	2·5	100 (100)	2·2 (1·7)
BOILED FOR 3 HR., 1·5 g. SODIUM SULPHATE PER LITRE										
1·94	—	—	67·8 (57·5)	2·1 (3·1)	82·8	0·6	—	—	97·7 (88·3)	1·2 (1·6)
2·2	83·7	1·1	69·7	3·2	84·2	1·4	96·5	2·7	95·6	1·6
2·6–2·7	88·9	1·1	80·8	2·1	92·8	1·6	99·1	1·8	99·4	2·1
2·8	86·4	1·7	75·9	1·6	85·2	1·6	99·6	2·8	94·8	1·8
3·0–3·1	86·8	2·8	74·8	3·1	—	—	101·5	2·9	91·7	0·5
3·1–3·2	92·8	1·3	74·9 (61·3)	1·0 (3·9)	88·9	2·0	99·0	2·4	91·3 (81·0)	2·7 (3·7)
3·8–4·3	88·0	0·9	79·1	2·0	—	—	99·2	2·7	86·8	0·6
4·4–4·5	87·7	1·4	78·6	2·8	—	—	102·1	2·5	90·7	1·9
5·0–5·2	88·9	0·8	72·6 (58·0)	1·8 (2·7)	—	—	99·4	3·7	87·2 (74·0)	1·6 (2·2)
5·9–6·0	85·0	1·7	70·7	2·6	—	—	99·3	2·3	87·3	2·3
BOILED FOR 3 HR., 0·0106 M. PHOSPHATE BUFFERS										
6·5–6·6	86·0	1·6	69·6	3·3	—	—	101·2	1·7	84·3	3·1
7·6–7·7	82·0	4·4	62·0 (49·2)	1·4 (2·6)	86·4	1·4	98·6	7·3	85·7 (68·4)	1·2 (3·0)
8·0–8·1	80·8	1·1	57·1	3·3	78·2	1·0	96·3	2·8	82·5	2·0
8·3–8·5	83·1	2·4	60·2 (49·7)	3·6 (1·8)	80·4	0·6	101·3	1·9	84·2 (70·8)	2·4 (1·5)
8·4–8·7	—	—	— (46·1)	— (4·2)	—	—	—	—	— (68·4)	— (3·0)
8·9–9·1	81·2	1·1	58·5	2·3	75·7	3·0	96·2	4·1	83·9	1·6

C.V. = Coefficient of variation of 5 measurements

is measured after the boiling treatment, and where loss of weight has occurred, e.g. at the extremes of the pH range, such loss will have the effect of inflating the bundle results as compared with those made on single threads, where the weight loss is not taken into account. The effect of boiling at either pH 2 or pH 6–7 has produced approximately equal losses in wet breaking load, and the maximum in breaking load at pH 3–4 is in good agreement with the results of Mosher[7] for the breaking load of hanks of worsted yarn after boiling for 2 hr. in

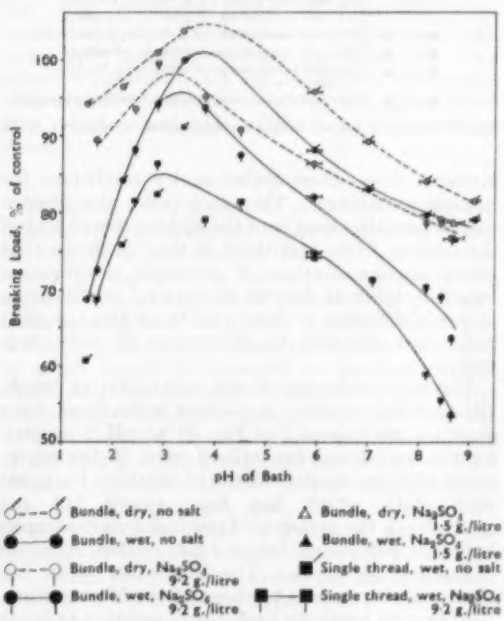

FIG. 3— Effect of pH of Boiling on Breaking Load of Yarns

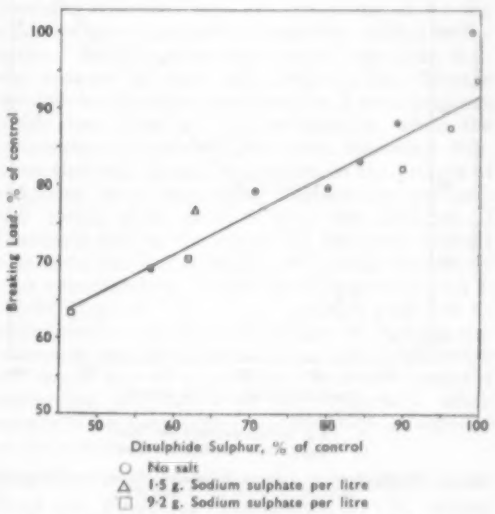

FIG. 4— Relation of Wet Bundle Breaking Load to Disulphide Sulphur in pH Range 3–9·2

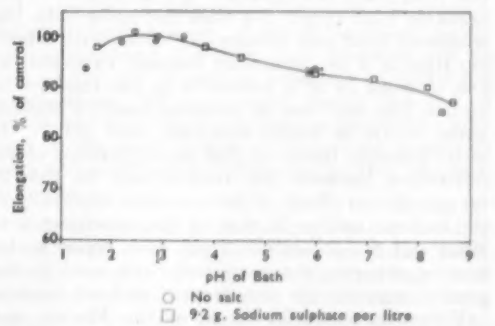

FIG. 5— Effect of pH of Boiling on Wet Single Thread Elongation at Break

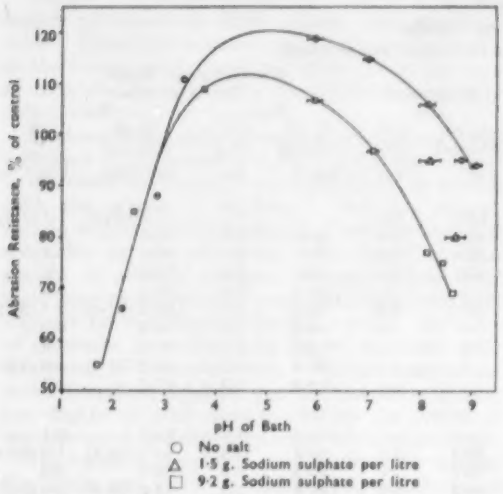

FIG. 6—Effect of pH of Boiling on Abrasion Resistance of Yarn

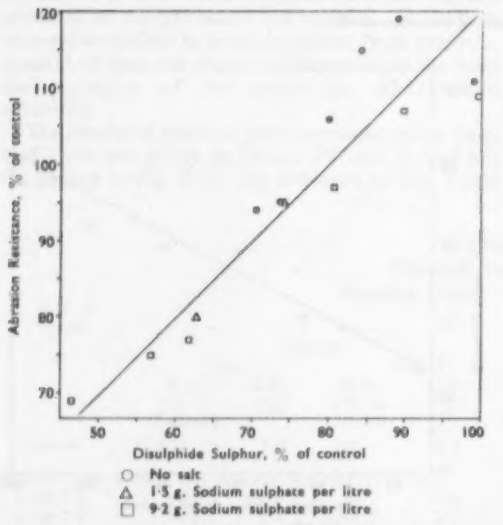

FIG. 7—Relation between Abrasion Resistance of Yarn and Disulphide Sulphur between pH 3 and 9·2

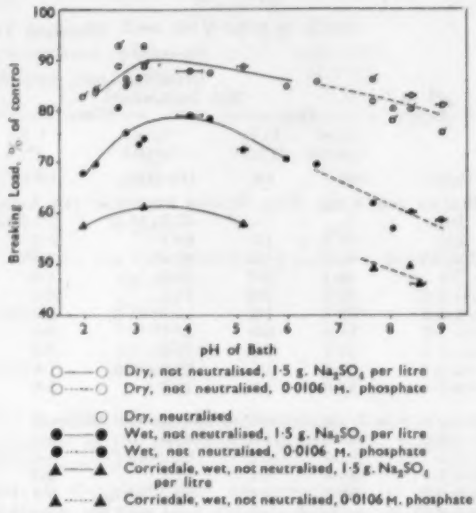

FIG. 8—Effect of pH of Boiling on Breaking Load of Cloth

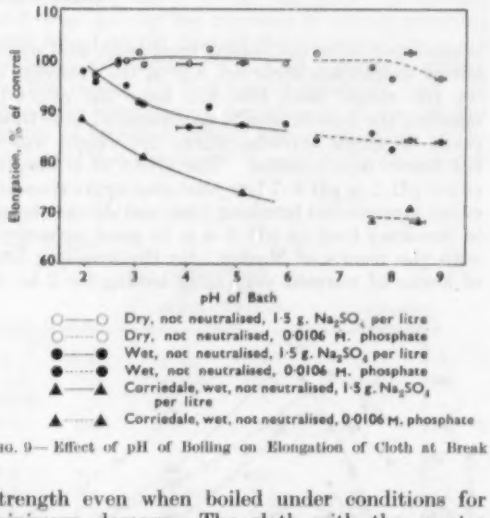

FIG. 9—Effect of pH of Boiling on Elongation of Cloth at Break

solutions held at pH values between 1 and 10. On the other hand the existence of a maximum in the breaking load at pH 3–4 does not agree with the results of Hind and Speakman [39] that, with a boiling time of 3 hr., minimum damage, expressed as loss of work of 30% extension in the instance of human hair and loss in breaking load for mohair yarn, occurs in buffer solutions near pH 7. It seems possible, however, that an explanation of the differences between the results may be due to (*a*) specific ion effects of the solutions, especially of the buffers; and/or (*b*) that in the experiments of Hind and Speakman the fibres were boiled under tension, whereas the yarn and cloth used in the present experiments were treated without tension.

When the breaking loads of the Merino and Corriedale cloths are compared, it is seen that the latter has shown considerably greater loss in strength even when boiled under conditions for minimum damage. The cloth with the greater loss in breaking load is of the tighter weave and of the coarser fibre, and there is thus evidence that either similar degrees of chemical modification result in different degrees of physical modification of wools differing in fibre quality or the apparent differences are due to differences in cloth construction.

The measurements of wet elongation at break, although less sensitive to changes in the fibres, have shown a maximum (see Fig. 5) at pH 3 approx. for the boiled and neutralised yarn, in fair agreement with the measurements of breaking load; but with cloth which has been rinsed but not neutralised, the presence of residual acid in samples boiled at pH values below 3 has caused increased elongation at break. The Corriedale cloth has shown similar trends to those of the Merino cloth, but, as with breaking load, the elongation at break is considerably smaller. The results for elongation

of dry cloth have given no indication of changes in the fibres except at the extreme pH values.

The relation of pH of treatment to the abrasion resistance of yarn is shown in Fig. 6. It is clear that no change in abrasion resistance has occurred as the result of boiling at pH values near 3, but between pH 3 and 7 increases of up to 20% have occurred, though their magnitude has been lessened by the presence of salt. It appears that the increase in abrasion resistance is associated with conditions of treatment which could result in supercontraction of the loosely held fibres, and so produce a more compact yarn better able to withstand abrasion. In contrast to the relationships found for wet breaking load, abrasion resistance has been found more sensitive to boiling acid solutions of pH below 3 than to boiling alkaline solutions.

Some indication that setting of the yarns has occurred during treatment was observed in the flattening, kinking, and loss of loftiness after boiling in the alkaline solutions. A few measurements of the power of the yarn (removed from the treated cloth) to supercontract [16], precautions being taken to prevent felting in the process of measurement, showed that, whereas the "control" yarn and yarn boiled at pH 3·1 supercontracted 28%, yarn boiled in alkaline buffer solutions supercontracted only 8%.

So far the results of chemical and physical measurements have been considered separately. When they are considered together, some degree of correlation is to be found between them. For treatments below pH 3 alkali solubility and soluble nitrogen, which may be considered to assess peptide hydrolysis, correlate well with wet breaking load, but the best correlation has been found with abrasion resistance, especially at pH values below 2·5. For treatments above pH 4 the disulphide content of the acid hydrolysate correlates well with wet bundle breaking load (see Fig. 4) and also with abrasion resistance (see Fig. 7), but the correlation with abrasion resistance is strong only after about 20% of the disulphide sulphur has been broken down.

DISCUSSION

The presence of a neutral salt, by reducing the difference between the pH of the solution surrounding the fibres and that of their internal solution, would be expected to increase respectively the amount of acid and alkali sorbed from acidic or alkaline solutions, as shown by Steinhardt and Harris [37]. At temperatures near 100°C. sorbed acid or alkali would be expected to produce peptide hydrolysis, but the experiments have yielded no conclusive evidence of this, except those at pH values below 3–4, in which, however, the addition of salt (9·2 g. sodium sulphate per litre) had little effect. In contrast to the relative stability of the wool towards hydrogen ions, the high sensitivity of the disulphide bond to hydroxyl ions is emphasised by the effect of salt above pH 6·8 and the occurrence of disulphide hydrolysis above pH 4.

While no comparable experimental results are available for the reaction of wool in alkaline solutions containing cations other than sodium, Korchagin's measurements [40] of the breakdown of silk fibroin in 0·02 N. alkali at 80°C. in the presence of neutral salts suggests that the reaction rate is related to the concentration, size, and charge of the cations. Thus at, say, pH 9 potassium ions would be expected to produce a higher alkali sorption in wool than the same concentration of sodium ions, though the difference in the effect of the cation would be expected to diminish as the isoelectric point of the wool is approached.

No definite evidence has been found of increased acid hydrolysis in the presence of sodium sulphate, and this suggests that its presence in concentrations used commercially is not a factor in producing damage to wool in acid dyeing. In drawing analogies with acid dyeing, however, it is well to bear in mind that high concentrations of anions of high affinity for wool, such as dyes and some textile auxiliary products, may produce peptide hydrolysis [41]. In dye liquors which become alkaline during boiling, it is clear that the possibility of alkali damage depends on other factors besides salt content. If strong alkali is produced, as for example in chroming, the amount of damage may be largely independent of the salt concentration, provided hydroxyl ions are not removed by the evaporation of ammonia or reaction with a buffer agent. But if escape of ammonia is possible, then the absence of salt will reduce alkali damage through keeping the concentration of hydroxyl ions inside the fibres as low as possible while the evaporation proceeds. The same reasoning indicates that salt should be avoided in the process of stripping with ammonia. Further, in commercial dyeing it is usual to base the addition of Glauber's salt on the weight of the wool without regard to the liquor ratio. Obviously, relatively high concentrations of salt can thus be produced in "short" liquors. While this practice may not be objectionable in the acid range of dyeing, unnecessary damage to the wool can arise from its use in "short" liquors of so-called "neutral" dyebaths containing alkaline wool, and especially when ammonia has been added to make the bath alkaline at the commencement of dyeing.

In view of the importance of disulphide breakdown in producing permanent set in animal fibres [11], it is to be expected from the relationships shown in Fig. 1 that setting solutions of the same pH value but of different salt content will produce different degrees of set. Some of the discrepancies in investigations of setting may therefore well be due to the use of setting solutions of undefined composition. In commercial dyeing the use of conditions which cause disulphide breakdown may lead to the development of permanent creases in yarn and cloth and probably also to fibre breakage in combing.

The influence of fibre swelling on the shearing forces tending to rupture fibres in cloths under tension would be expected to increase with increased tightness of weave. It has already been mentioned that, for a given boiling treatment, the tightly woven Corriedale cloth showed a much greater loss of wet breaking load than did the

Merino cloth. The chemical damage was practically the same in both cloths, but a large loss of wet breaking load was found in the Corriedale cloth even after boiling under conditions for minimum chemical damage. Thus there is some evidence that increased swelling capacity in water has been given to wool by boiling under the mildest conditions, which, though giving no definite evidence of chemical damage by the methods available, would seem to have disorganised the crystalline portion of the keratin.

It is not suggested that wool dyed at the same pH value and for the same time will undergo changes in properties identical to those produced in one of the present experiments. Allowance would need to be made for the modifying effects of dye, lake, and mordant on the physical properties of wool, but it seems neither likely that these effects would be large in pale shades nor probable that the breakage of peptide and disulphide bonds would be entirely prevented by these agents. The presence, however, of tervalent chromium within the fibre in excess of the amount required for lake formation would, by the production of new cross-linkages [42], be expected to have a strengthening effect. Finally, the fact that the temperature in commercial dyeings does not normally exceed 95–98°C. suggests that the commercial processes would be less damaging than is indicated by the present experiments. The results of Mosher [7] for the breaking loads of worsted yarn after treatment for 2 hr. at 90°C. and 100°C. respectively show, however, that the difference in strength is not large.

CONCLUSIONS

The examination of wool after boiling treatments in water and sodium sulphate solutions in the pH range 1·5–9 for 3 hr. has led to the following conclusions—

(1) The consensus of the evidence from determinations of disulphide sulphur, total sulphur, alkali solubility, soluble nitrogen, loss in weight, breaking load, elongation at break, and abrasion resistance has shown that the wool has suffered minimum modification when boiled at pH 3–3·5

(2) Sodium sulphate, in concentrations up to 9·2 g./litre, has shown relatively little effect on the wool within the pH range 1·7–6·8, but above pH 6·8 the presence of sodium sulphate has caused alkali damage, which increases rapidly with increase of salt concentration and rise of pH.

(3) A strong correlation has been found between the disulphide sulphur content of the acid hydrolysate and the wet breaking load of yarn and cloth after boiling in solutions having pH values above 4. A similar correlation, but applying only after about 20% of the disulphide sulphur has been broken down in the boiling process, has been found between disulphide sulphur content and abrasion resistance.

(4) The alkali solubility and soluble nitrogen tests have shown a strong correlation with abrasion resistance and to a lesser extent with wet strength after boiling in solutions having pH values below 2·5.

(5) The total sulphur content, though showing a similar trend to the content of disulphide sulphur, has been found relatively insensitive as a measure of alkali damage.

* * *

The author desires to thank Mr. J. Barritt and Dr. F. F. Elsworth for much helpful advice in connection with the experimental work and the preparation of the manuscript, and Mr. S. L. Anderson and his staff for carrying out many of the physical measurements. The assistance of Mr. R. F. Pickup in the analytical work is gratefully acknowledged. Thanks are also due to the Director and the Council of the Wool Industries Research Association for permission to publish this paper.

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(*Received 18th July 1953*)

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ERRATA

Mélange or Vigoureux Printing, by F. BUXTORF and A. WIAZMITINOW (J.S.D.C., **69** (Dec. 1953))—

Page 551— In the recipe, the strength of the ammonium tartrate should be 1 : 2, as on p. 554.

Page 553— In the first recipe the brace should enclose also the ammonium oxalate.

Page 554— In the first recipe in the second column, the figures for water and sodium phosphate should be—

335–295 Hot (200°F.) water
15–15 Sodium phosphate

The Heat Setting of Terylene Polyester Filament Fabrics in relation to Dyeing and Finishing. by D. N. MARVIN (J.S.D.C., **70**, 19 (Jan. 1954))—

The ordinates of Fig. 7 should read—

Bending Length 2° 2·5° 3°

Notes

Nomination of President-elect

Council has unanimously nominated Mr. Fred Smith for election as President-elect for 1954–1955. Mr. Smith will thus become the first President of the Society to have served on a Junior Branch Committee, since he was Chairman of the Bradford Junior Branch from 1920 to 1925.

Fifty Years' Membership

The following members—Messrs. A. Highley, H. Levinstein, F. Scholefield, G. E. Knowles, H. Wilkinson, and H. Yeoman—have completed fifty years of membership. Council wishes to congratulate them on this notable achievement, and looks forward to their continued interest in the Society for many more years.

Meetings of Council and Committees

January

Council— 13th
Finance— 13th and 25th
Publications— 19th
Fastness Tests Co-ordinating— 26th
Diploma— 28th
Colour Index Editorial Panel— 14th

Death

We regret to report the loss by death of Mr. J. C. Hamilton.

Tentative Definitions

The Terms and Definitions Committee will welcome comments on the following tentative definitions—

47. VIGOUREUX PRINTING

See "Mélange Printing".

49. AGEING

Originally a process in which printed fabric was exposed to a hot moist atmosphere. At the present time the term is almost exclusively applied to treatment of printed fabric in moist steam in absence of air.

Ageing is also used in the development of certain colours in dyeing, e.g. aniline black.

50. AGER

A steam chamber used for ageing printed or padded cloth.

51. ACID AGEING

Ageing in which a volatile acid is also present in the vapour around the fabric.

52. BARRY

A term applied to faulty fabrics which exhibit light and dark weft bars originating in (*a*) lustre differences, (*b*) slight differences in dyeing affinity, or (*c*) differences in pick spacing.

53. BLEEDING

(*a*) Loss of dye from a coloured fabric when immersed in water or solvent, leading to an obvious coloration of the liquor.

(*b*) Spreading of dye from a portion of a printed design to contiguous areas.

54. BLINDING

Marked and undesirable loss of lustre of fibres after wet processing. This may be due, for example, to the formation of dye or other particles within or on the fibre, which scatter light.

55. CARRIER

Any auxiliary product added to a dyebath to promote dyeing of hydrophobic fibres, and characterised by affinity for, and ability to swell, the fibre.

56. CHEMICKING

Bleaching non-protein fibre materials by means of a dilute hypochlorite solution.

57. CLEARING

(*in printing*)

A mild bleaching treatment applied to printed fabrics with the object of removing traces of unwanted dye from, and improving the whiteness of, the uncoloured areas.

58. DEVELOPING

A stage in dyeing or printing during which leuco compounds, dyes, or dye intermediates are converted by chemical reaction into stable dyes within the fibre.

59. DISCHARGE

Destruction by chemical means of a dye or mordant already present in a fibre.

University College of North Staffordshire

Research Fellowship for Fundamental Investigations into Inorganic Colouring Matters

The Blythe Colour Works Ltd., Cresswell, North Staffordshire, has founded a fellowship in chemistry for the support of fundamental investigations into inorganic colouring matters, the first holder of the fellowship being Dr. S. C. Nyburg, an assistant lecturer in the Department of Chemistry. C O C

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Squeeze Rollers. E. Küsters. *BP* 700,436

Squeeze rollers of diameter > 120 mm. are supported by other rollers placed along the length of the squeeze rollers. By this means the squeeze rollers form an obtuse entry angle and make line contact instead of surface contact with one another. Owing to this obtuse angle formation of a water wave which can be carried into the entry between the rollers is prevented so that the machine can work at increased speed. In addition the specific pressure of the rollers against one another is greater because it is no longer distributed over a large area. The supporting rollers prevent bowing of the squeezing rollers thus rendering it unnecessary for them to be curved with the result that the machine can work at any pressure and so on any kind of fabric. C. O. C.

Thread Advancing and Storage Reels. American Viscose Corpn. *USP* 2,628,406–10 C. O. C.

Thread Advancing and Storage Reels. Industrial Rayon Corpn. *USP* 2,628,411

Wetting, Stretching and Drying Yarn to increase its Tensile Strength. Specialities Development Corpn. *USP* 2,628,405

Apparatus to carry out the process of *USP* 2,220,958 in which yarn is impregnated with a bonding agent, stretched and dried under tension. C. O. C.

Guiding Fabric etc. into Drying Machines or the like. Aktiebolaget Svenska Fläktfabriken. *BP* 700,857

A device to eliminate the "hunting" effect of the feelers, selvedge guides, etc. C. O. C.

Dielectric Heating. J. B. Cunningham and F. Wilburn. *BP* 700,467–8

Very high frequency energy, e.g. ca. 90 megacycles, is especially useful when properly applied in the heating and drying of thin films. The proper application of this energy involves the factors of high energy or field intensity and uniformity of fields. Suitable apparatus is described. C. O. C.

Minimising the Shrinkage of Fabric during Treatment at High Temperatures. I.C.I. *BP* 700,100

The fabric is passed over a heated drum while being held taut by at least two sets of pins placed round the drum. C. O. C.

Drum Washing Machine. A. E. Chapman. *BP* 699,794

A machine which does not require a heavy concrete or like foundation and which washes effectively at low speeds. C. O. C.

Automatically Controlled Dry Cleaning Apparatus. Elma Aktiengesellschaft für Maschinenbau & Chemie. *BP* 700,634

The apparatus is controlled by a multi-way cock which opens or closes various paths of flow for the several liquids consecutively in the chronological sequence required in the cleaning operation. C. O. C.

Laundry Ironing Machine. G. Vercammen. *BP* 700,069

The goods pass between an iron cylinder and a counter-member, both of which are heated by gas. C. O. C.

Laundry Pressing Machine. L. Shippey and A. Denison. *BP* 700,861

Improved mechanism for rotating the turntable after each pressing operation when the ram is withdrawn. C. O. C.

Garment Steaming and Pressing Machine. Rayplate Corpn. *BP* 700,331

A press plate for the head of a garment pressing machine is etched or sandblasted to give it a roughened surface similar to that of No. 48–80 emery cloth. It not only eliminates shine but leaves no undesirable impression on the garment. C. O. C.

II—WATER AND EFFLUENTS

Iron Treatment of Waste Liquors containing Dyes—I. M. Kehren and J. Thewis. *Melliand Textilber.*, **34**, 770 (Aug.); 863–865 (Sept. 1953).

The Niers process, using cast-iron shot and ferrous sulphate, works satisfactorily on the small or large scale. The iron treatment is discussed theoretically and some experiments on the coagulation of Indigo Carmine soln. are reported. H. E. N.

PATENT

Recovery of Wool Grease from Spent Scouring Liquor. Pacific Mills. *BP* 700,215

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Silicones—Investigation of Possible Uses. R. Schweiger. *Melliand Textilber.*, **34**, 344–345 (April); 543–545 (June 1953).

Samples were prepared by treating *cotton* poplin with W8-60 (I) and De Cetex 104 (II; Wacker, Munich), with a wax-emulsion (Hydrophobol WF; III), and a condensate (Persistol NO; IV) according to the recommended procedures. These samples were used for a preliminary evaluation. Wetting, penetration, and absorption of water are less favourable for I and II, than for III, but their resistance to washing and rate of drying is higher. I and II offer slightly more resistance to air than III or IV. The tenacity of the yarns is lower for I and II than for III and IV, but their extensibility is a little greater. Resistance to abrasion is better for I and II than for IV. There was no great difference in fastness to light of 3 dyeings treated with I, II, III, or IV. The results permit no definite conclusions, but encourage further investigation. Owing to losses by volatilisation, ashing is unsatisfactory and silica from silicone finishes is best determined by warming with H_2SO_4, adding HNO_3 dropwise, and evaporating. H. E. N.

PATENTS

Organotrihalogenosilanes—Intermediates for Wetting Agents. Cowles Chemical Co. *BP* 700,553

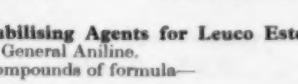
The hydrolysates of alkylphenyltrichlorosilanes containing one or two straight-chain Alk substituent groups of 4–12 C or of an alkylbenzyltrichlorosilane having one or two straight chain alkyl substituent groups of 1–12 C are very efficient wetting agents in aqueous soln. The number of carbon atoms attached to the aromatic nucleus has an important effect, thus the wetting effect of the alkylbenzyl derivatives is significantly greater than that of the benzyl derivatives. C. O. C.

Dizinc Salt of Hydroxymethanesulphinic Acid. Basf. *BP* 701,020

A particularly pure product is simply obtained by reacting sodium hydroxymethanesulphinate in aqueous solution with a zinc salt (preferably an inorganic salt) and precipitating the dizinc salt of the hydroxymethane sulphinic acid by bases, preferably inorganic bases, while keeping at low temperature, preferably < 30°C. C. O. C.

Solubilising Agents for Leuco Esters of Vat Dyes. General Aniline. *USP* 2,628,882

Compounds of formula—



(n = 0–4; Z = atoms to complete a pyridine, C-alkylpyridine or quinoline radical; the SO_3^- group is present either in the phenyl ring or in the heterocyclic radical) are effective solubilising agents in printing pastes for leuco esters of vat dyes. C. O. C.

Gas-fading Inhibitors. BrC. *BP* 700,369

Alkali metal phthalates are excellent gas-fading inhibitors which do not adversely affect the fastness to light of acetate or direct cotton dyes. C. O. C.

Ageing. R. W. Jacoby. *USP* 2,628,884

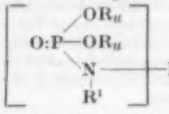
Improvement of *USP* 1,663,845. A much greater volume of steam is directed about the fabric where ageing commences in order to more readily absorb the heat given out when reduction commences. C. O. C.

Acid Catalysts for Resin Finishes, etc. Henkel & Cie. *BP* 700,118

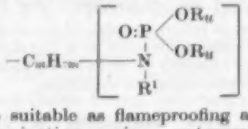
Polychlorinated hydroaromatic ketones containing > 3Cl per molecule act as acid catalysts for aldehyde condensates with urea, melamine, etc. when heated to < 70°c. They are stable and exert no catalytic effect below this temperature. C. O. C.

Dialkene Phosphonamides and their Derivatives as Flame- and Waterproofing Agents, Coatings, etc. Glenn L. Martin Co. *BP* 699,951

The products specified in *BP* 688,372 and the halogenated polymerisation products of compounds of formula—



(R_u = unsat. aliphatic radical of 3–5C; R^1 = H, Alk. of 1–3C, hydroxalkyl of 1–3C, or an unsat. aliphatic radical of 3–5C; R^2 = unsat. aliphatic radical of 3–5C or



(m = 1–3)) are suitable as flameproofing agents and as plasticisers, laminating resins, waterproofing agents, coatings, corrosion inhibitors, insecticides and fungicides. *BP* 700,455

The monomers of the above dialkene phosphonamides and their halogenated derivatives are excellent flameproofing agents where permanency is not required. C. O. C.

Brominated Alkene Phosphates as Flameproofing Agents. Glenn L. Martin Co. *BP* 700,292

Modification of *BP* 688,372.

The brominated products are more efficient flameproofing agents than the chlorinated, the latter act merely as flame retardants while the brominated products are excellent flameproofers particularly when there are 2 Br atoms on adjacent carbon atoms. Leaving at least one double bond of the original unsaturation of the monomer intact appears to give better affinity for the fibre. C. O. C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Dyeing of Synthetic Fibres. I—Azo Dyes for Vinylon (Polyvinyl Alcohol) Fibres. S. Yoshikawa, S. Kojima and E. Minami. *Bull. Osaka Ind. Research Inst.*, **3**, 49–52 (1952): *Chem. Abs.*, **47**, 10855 (25 Oct. 1953).

Benzidine was tetrazotised in HCl with $NaNO_2$ at < 5°c. and then coupled with α-naphthylamine at room temperature overnight and 50–55°c. for 3 days to yield dye No. 1—$R^1N{:}NC_6H_4C_6H_4N{:}NR^2$ (R^1 and R^2 = 1-aminonaphthyl). Dyes No. 2 and 3 were similarly obtained by using tolidine and dianisidine respectively. Other dyes were all synthesised from benzidine by general or specific methods. Thus in dye No. 4, R^1 and R^2 = 2-aminonaphthyl; in dye No. 5 R^1 = 1-aminonaphthyl and R^2 = Na salicylate; in dye No. 6 $R^1 = C_6H_3(NH_2)_2$ ($N{:}NC_6H_5$) and R^2 = H; in dye No. 7 R^1 = Na salicylate and R^2 = H; in dye No. 8 R^1 = 2-hydroxynaphthyl and R^2 = H. These dyes contain no SO_3H, are hydrophobic, and (except for No. 7 and 8, which dispersed poorly) gave good orange to red dyeings on vinylon from an aqueous methylalcohol bath. The NH_2 radical seemed to contribute to good dyeing. C. O. C.

Changing Aspects of Pearl Essence Technology. W. E. Decker. *Org. Finishing*, **14** (7), 11, 13 (1953): *Chem. Abs.*, **47**, 10767 (25 Oct. 1953).

A review of past work on the recovery and use of pearl essence. Pearl essence from fish scales is largely composed of guanine crystals sheathed in an envelope of protein hydrolysate material. Recent work reverses the approach to the problem of recovering the guanine crystals from fish waste. In the new method the guanine is dissolved, filtered and recrystallised after addition of an appropriate colloid to the liquor. Crystal size is controlled by regulating temperature and concentration. This makes possible a uniform supply of colloid-coated guanine crystals that are more brilliant than the best grade of natural pearl essence recovered from fish scales. C. O. C.

Utilisation of Silkworm Fæces as Dyes and Pigments. K. Tomizuka. *J. Sericult. Sci. Japan*, **19**, 189–191 (1950): *Chem. Abs.*, **47**, 10854 (25 Oct. 1953).

The hot-water extract of silkworm fæces was used to dye various animal fibres, most profitably for silk fixed with sericin, rich colours of good fastness. Useful lakes were obtained by extracting the fæces with $SnCl_2$, $CuSO_4$, Pb acetate and with Pb acetate together with $K_2Cr_2O_7$. The tin lake was insoluble in 94% alcohol and in $CHCl_3$ but soluble in 30% NaOH and H_2SO_4 (d. 1·84). C. O. C.

Inorganic Pigments. IV. Cobalt Arsenate. 1. Compositions and some Properties of Cobaltous Arsenates obtained by the Wet Process. T. Ando and S. Minami. *Bull. Osaka Ind. Research Inst.*, **3**, 44–9 (1952): *Chem. Abs.*, **47**, 10866 (25 Oct. 1953).

Adding various amounts of 5% $Na_2HAsO_4,7H_2O$ to 5% $Co(NO_3)_2,6H_2O$ resulted in precipitation of $Co_m(AsO_4)_2,xH_2O$ (m is inconstant but ca. 2·5). This precipitate when calcined and then dipped in water changed to $Co_3(AsO_4)_2,8H_2O$ with liberation of H_3AsO_4 and was dehydrated gradually by heating with no change in the Co : AsO_4 ratio. A 0·1% mixture similar to the above (here $CoSO_4,7H_2O$ could be substituted for the nitrate) was used to get another arsenate having the same formula as the above. Upon heating both these arsenates lost about half their water of crystallisation at 180–200°c. X-Ray examination of the three cobalt arsenates showed the same structure but that from the 0·1% mixture had the best colour when made into a pigment by roasting. C. O. C.

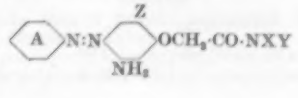
PATENTS

Azoic Dyes—Preparation of β-Naphthylamides of o-Hydroxyarylcarboxylic Acids. Ciba. *BP* 700,024

To avoid the danger to health involved in handling β-naphthylamine, o-hydroxyarylcarboxy-β-naphthylamides are made by condensing an o-hydroxyarylcarboxylic acid or acid halide with 2-naphthylamine-1-sulphonic acid, the sulpho group being split off during the reaction. Thus, 2-naphthylamine-1-sulphonic acid, prepared from ammonia and 2-naphthol-1-sulphonic acid, is added to a mixture of 3-hydroxy-2-naphthoic acid and aq. NaOH in toluene. After driving off water, PCl_3 is run in at 75–85°c., followed by refluxing for 8 hr. The reaction mixture is then made alkaline with soda ash and the toluene, as well as some β-naphthylamine formed during the reaction, removed by steam distillation. E. S.

Azoic Dyes—Diazotisable 2-aminoazobenzene Derivatives. FH. *BP* 699,761

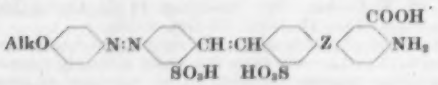
2-Aminoazobenzene derivatives—



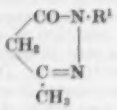
(X, Y, and Z = Alk; A may contain substituents common in azoic bases) may be diazotised in relatively dilute mineral acids (unlike 4-alkoxy-2-aminoazobenzenes, which need concentrated hydrochloric or sulphuric acid for successful diazotisation), and give diazonium compounds of adequate solubility. Thus, all parts being by weight, 2-amino-5-methyl-2′-chloro-4′-nitroazobenzene-4-oxyacetdiethylamide (42·4) may be diazotised in 17·7% aq. HCl(600) at 15–20°C. and the resulting diazonium chloride solution used in the preparation of the zinc chloride double salt. E. S.

Metallisable Stilbene Azo Direct Cotton Dyes. Ciba. *BP* 700,210

The diazo compound of an aminoazo compound—



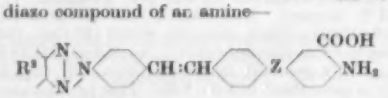
(Z = azo or azoxy) is coupled with a pyrazolone—



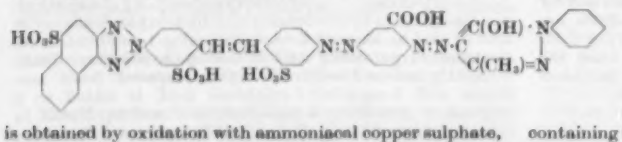
(R^1 = a residue containing two benzene rings, one ring attached directly to the N atom of the pyrazolone, and the second ring attached to the *m*- or *p*-position of the first ring, if desired by means of a bridge member) to give direct cotton dyes which may be treated in substance, or preferably in the dyebath or on the fibre with metal (especially copper) salts. Thus the monoazo compound 4-amino-4′-nitrostilbene-2:2′-disulphonic acid → phenol is *O*-methylated, and then boiled with 2:5-diaminobenzoic acid in presence of aq. NaOH. The product is diazotised and coupled with 3-methyl-1-*p*-phenylphenyl-5-pyrazolone, to yield a red-orange dye applicable to cotton by the single- or two-bath aftercoppering process.

BP 700,211

The diazo compound of an amine—



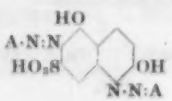
(R^2 = a naphthalene residue; Z = azo or azoxy) is coupled with a 5-pyrazolone to yield direct cotton dyes which may be treated in substance or on the fibre with copper salts. The treatment in substance is suitable if the complex so produced has sufficient solubility, such as is generally conferred by the presence of four sulpho groups in the dye molecule; if fewer solubilizing groups are present, treatment in the dyebath or on the fibre is generally preferable. Thus diazotised 4-amino-4′-nitrostilbene-2:2′-disulphonic acid is coupled with the *ω*-methanesulphonic acid of anthranilic acid, and after splitting off the *ω*-methanesulphonic residue, the aminoazo compound so produced is diazotised and coupled with 3-methyl-1-phenyl-5-pyrazolone. The nitro group is then reduced to amino with Na_2S, and a trisazo compound formed by diazotising and coupling with naphthionic acid. The triazole compound—

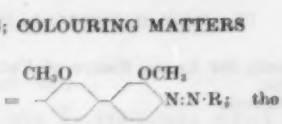


is obtained by oxidation with ammoniacal copper sulphate, and freed from copper with hot 4% HCl. It dyes cotton orange by the single- or two-bath aftercoppering process. E. S.

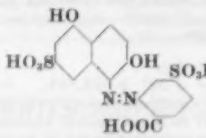
Navy Blue and Grey Metal (Copper)-complex Polyazo Direct Cotton Dyes. S. *BP* 700,229

Copper complexes derived from polyazo dyes—





(one A = ; the other A = aryl carrying COOH or OCH_3 *ortho* to the azo link; R = the residue of a mono- or di-hydroxynaphthalene-mono-, di-, or tri-sulphonic acid coupled *ortho* to the OH group, or = the residue of an aminonaphtholmono- or di-sulphonic acid which may be *N*-alkylated, -arylated, or -acylated) are navy blue and blue-grey direct cotton dyes. During the coppering process *o*-methoxy groups are demethylated. Thus, tetrazotised *o*-dianisidine is coupled first with an alkaline solution of 1-naphthol-3:8-disulphonic acid and then with a solution of the monoazo compound—



in ammoniacal pyridine. Coppering is carried out with ammoniacal copper sulphate in presence of diethanolamine to yield the navy blue direct cotton dye. E. S.

Metal(Chromium and Cobalt)-complex Azo Dyes for Wool, etc. Ciba. *BP* 699,976

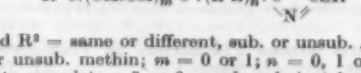
The cobalt, or preferably chromium, complexes containing 1 atom of metal to 1 mol. of each of two different monoazo compounds free of sulpho and carboxy groups dye animal and polyamide fibres from weakly acid baths. One or both of the component monoazo compounds contain a sulphamyl group, and at least one nitro group is also present. Thus, all parts being by weight, a mixture of the monoazo compounds 2-amino-4-nitrophenol→*p*-cresol (2·95) and 2-amino-6-chloro-4-nitrophenol→3-methyl-1-*p*-sulphamylphenyl-5-pyrazolone (4·74) is refluxed with aqueous sodium-potassium chromosalicylate (25) of Cr content 2·6% containing sulphonated castor oil (6). The sodium salt of the resulting complex is water-soluble and dyes wool orange-brown. E. S.

7-Diethylamino-4-methylcoumarin for Identifying Cellulose Ester Films bearing a Photographic Emulsion. Kodak. *BP* 700,646

Incorporation of 0·0001–0·0002% of 7-diethylamino-4-methylcoumarin in cellulose ester films used as a base for photographic emulsions results in a purplish fluorescence when the film is exposed to ultraviolet radiation and has no effect on the photographic emulsion. C. O. C.

***mero*Cyanine Dyes containing a 2-Alkylthio-5-thiazolone Nucleus.** Kodak. *BP* 700,734

Dyes of formula—



(R^1 and R^2 = same or different, sub. or unsub. Alk; L = sub. or unsub. methin; *m* = 0 or 1; *n* = 0, 1 or 2; Z = atoms to complete a 5 or 6 membered ring) have photographic sensitising properties. C. O. C.

Extraction, Concentration, and Stabilisation of Carotene. H. Schoppe & Schultz. *BP* 700,509

A product suitable for colouring butter etc. is obtained by finely disintegrating fresh carrots and emulsifying them with an oil or fat and then isolating the oil or fat phase containing the carotene from the water and the solid phases. C. O. C.

Carbon Black. Godfrey L. Cabot. *USP* 2,628,891

Apparatus which gives larger yields of channel black. C. O. C.

Bronze Powders. Canadian Bronze Powder Works. *BP* 699,983

The resistance to tarnishing and discolouration of copper-based bronze powders is increased by heating them to 600°C. in an atmosphere having no decarbonising properties, e.g. in propane. C. O. C.

Deep Maroon Copper Ferrocyanide Pigment. Interchemical Corpn. *BP* 700,476

A clear bright maroon pigment of potassium content within ± 2·0% of that for K_2 Cu Fe(CN)$_6$ and of particle size 0·03–0·5 μ is obtained by reacting 25% aqueous solutions of copper sulphate and potassium ferrocyanide at < 75°c. preferably at 100°c. taking care that the ferrocyanide is always in stoichiometric excess of that necessary to react with the copper sulphate to form the pigment. C. O. C.

Red Luminescent Material. British Thomson-Houston Co. *BP* 699,847

A mixture of precipitated cadmium phosphate, zinc fluoride and a manganese activator when fired for < 1 hr. yields a phosphor which emits red light when exposed to ultraviolet radiation. C. O. C.

Red Lead. Société Solumeta. *BP* 701,187

Lead vapour is mixed with air, which may be enriched with oxygen, through a reaction zone in an almost horizontal direction. This enables continuous production of a finely divided product of high Pb_3O_4 content. C. O. C.

Titanium Dioxide. American Cyanamid Co. *USP* 2,628,919

Titanium dioxide is freed from soluble salts and all but traces of free polyvalent cations by dispersing it in water and then flocculating it by adding a barium compound. C. O. C.

Acid-resistant Ultramarine. American Cyanamid Co. *USP* 2,628,920

Ultramarine is treated with very dilute sulphuric acid, heated with an aqueous solution of sodium silicate and then calcined to yield a product of extraordinary resistance to acid. C. O. C.

Diazotype Developers containing Fluorescent Brightening Agents (IX p. 99).
Titanium Dioxide as a Pigment for Coated Papers and its Detection in Paper (XIV p. 102).
Chromatography and Synthesis of Polymethinic Dyes (XIV p. 103).

V— PAINTS; ENAMELS; INKS

PATENTS

Film-forming Composition in Gel. Form. P. Mahler. *BP* 700,179

A film-forming composition consists of a liquid hydrocarbon, a water-insoluble soap of tall oil and a solubilising agent together with pigments, extenders, etc. C. O. C.

Micaceous Iron Oxide Paint. Duisburger Kupferhütte. *BP* 700,431

Addition of lead cyanamide to micaceous iron oxide paints almost entirely prevents settling out and thickening. It also allows such paints to be produced in bright colours, e.g. red or green, with a semi-gloss finish. C. O. C.

Coated Polystyrene (XIII p. 101).

VI— FIBRES; YARNS; FABRICS

Impurities on Textiles. E. Götte. *Melliand Textilber.*, **34**, 754–755 (Aug. 1953).

A review of the nature of the foreign substances in the raw fibre and those taken up during processing and use. The power of adhesion of dirt is considered. 30 references. H. E. N.

Flock Effects. C. Reisinger. *Melliand Textilber.*, **34**, 656–657 (July 1953).

The electrostatic apparatus and process are described. H. E. N.

Velvets Electrostatically Produced (Flocking). W. Steinberg. *Melliand Textilber.*, **34**, 536–537 (June 1953).

An adhesive, usually an aq. dispersion of polymerised acrylic esters, is applied to cloth, preferably of cotton or man-made fibres, by screen or roller printing, or by means of a doctor if the whole surface is to be treated. Flock, best 0·5–1 mm. long, 3 or 6 denier, containing about 12% moisture, is applied by a special electrostatic device. Excess flock is removed by suction, the adhesive is hardened at 110–140°c., and the material is thoroughly brushed. H. E. N.

Bonding Fibres to the Fabric Surface. R. Günther. *Melliand Textilber.*, **34**, 333–335 (April); 446–448 (May 1953).

A review with 24 references, covering the choice of basic fabrics, adhesives, and machines (including flock-printing). H. E. N.

Effect of Sonic Vibrations on Fibrous Materials. H. Rath and H. Merk. *Melliand Textilber.*, **34**, 653–656 (July); 763–765 (Aug. 1953).

Ultrasonic vibrations cause damage only when cavitation occurs. As cavitation and formation of bubbles depend on the frequency, becoming greater with lower frequencies, damage to fibres is observed only with vibrations of lower frequency (10 kilocycles/sec.). Cellulosic fibres, particularly bast fibres, disintegrate in fields of standing waves, when gas bubbles are formed through resonance. Wool and Perlon appear unchanged. Yarns, unless of wool, are severely damaged, but woven material disturbs the standing waves, hardly comes into contact with the bubbles and so is practically unaffected. 16 references and 28 photomicrographs. H. E. N.

Methods of Improving Natural and Artificial Fibres. A. Sippel. *Melliand Textilber.*, **34**, 433–435 (May 1953).

A review with 36 references. H. E. N.

Stretching and Breaking of Bast Fibres. F. Tobler. *Melliand Textilber.*, **34**, 746–747 (Aug. 1953).

During stretching but before breaking bast fibres exhibit cracks and deformities. Broken fibres show brush-like ends. These phenomena are discussed and illustrated by 4 photomicrographs. H. E. N.

Ramie. R. A. Denis. *Melliand Textilber.*, **34**, 399–401 (May); 493–494 (June); 615–617 (July); 817–818 (Sept. 1953).

A full description of the two types of plant, their fibres, their cultivation and processing prior to spinning, together with essential statistics. The average tenacity of ramie is 6·4 g./denier; the extension at break is 2·0–2·2%. H. E. N.

Methods of Preparing Kenaf. C. G. Hof. *Melliand Textilber.*, **34**, 263 (April 1953).

Kenaf Retting. R. Otto. *Melliand Textilber.*, **34**, 710–712 (Aug. 1953).

A comparison of biological and chemical methods leads to preference of the former, which is discussed in detail. 15 references. H. E. N.

Fibre of the Dwarf Palm of French Morocco. F. Reichel. *Melliand Textilber.*, **34**, 402 (May 1953).

Microbial Attack of Grège Silk. W. Wegener and R. Questel. *Melliand Textilber.*, **34**, 403–404 (May); 494–499 (June 1953).

After being exposed for 3 years in a deep, dark, damp cellar (70–90% R.H.; 5–15°c.), the raw silk was sorted into 4 grades according to the degree of damage, and then kept in a desiccator (92% R.H.; 25°c.) for a further 18 months. During the latter period it was examined repeatedly by physical methods and by shaking off micro-organisms on to sterilised agar. The breaking strength falls off considerably during the first months and, together with the tearing time and the elongation at break, decreases more or less with time. The pH varies less. The microbes present are identified and their rhythm recorded: the bacteria show maxima every 39 days, the *Penicillium* and *Aspergillus* species exhibit similar periodicity, but their maxima occur when the bacteria are at a minimum. Fungi imperfecti have a different rhythm, whereas the *Mucor* species occur only sporadically. 42 phase-contrast photomicrographs illustrate the agar forms of some fungi on sericin, the degenerate forms on fibroin, and the various stages of tendering. H. E. N.

Influence of Drawing on the Physical Properties of Perlon. H. Böhringer. *Melliand Textilber.*, **34**, 712–713 (Aug.); 822–823 (Sept. 1953).

Graphs illustrate the effect of stretching during spinning and during drawing upon the sp. gr., breaking length, load and extension at break, and similar properties. The specific elastic work of rupture is found to exhibit a maximum. H. E. N.

PATENTS

Acrylonitrile Fibres having Increased Affinity for Dyes. Chemstrand Corpn. *BP* 700,565

Blended polymers of a major proportion of a non-dyeable acrylonitrile polymer and a minor proportion of a vinyl-

pyridine or an alkyl substituted vinylpyridine polymer dissolve in conventional solvents for acrylonitrile polymers to produce solutions of unusual homogeneity and spinnability if a little sulphuric acid or an alkyl ester of an aromatic sulphonic acid is present. Fibres from such solutions have increased affinity for dyes. C. O. C.

Increasing the Hot-strength and Affinity for Dyes of Polyacrylonitrile Fibres. FBy. *BP* 700,172

Treating polyacrylonitrile fibres with ammonia or an aliphatic amine or a solution of the latter in an inert solvent increases both their tensile strength when they are heated and their affinity for dyes, particularly acid dyes. C. O. C.

Accelerated Oxidation of Cotton Cellulose in Presence of Reducing Agents. II. S. H. Mhatre, G. M. Nabar and G. M. Vyas. *Proc. Indian Acad. Sci.*, **32A**, 319–329 (1950): *Chem. Abs.*, **47**, 10856 (25 Oct. 1953).

A study of the relationship between the pH of NaOCl soln. and the amount of O consumed at 30°c. by cotton in presence of $Fe(OH)_3$ or various leuco vat dyes of different chemical structural groups. The rate and amount of O uptake and the pH of maximum O uptake by cellulose depend on the reducing agent present in the fibre during NaOCl treatment. Although the relation between pH and corrected oxidation potentials of NaOCl soln. at 20°c. resembles the relation between pH and O uptake of the cellulose, it does not do so at 30°c. and no general linear relation exists between the corrected oxidation potentials and O transfer. C. O. C.

Reducing the Tendency of Polymers to accumulate Electrostatic Charges (XIII p. 101).
Heat Stabilisation of Polyamides (XIII p. 102).
Chemical Determination of Amino Groups in Polyamides (XIV p. 102).

VIII—DYEING

Colour—Dyes—Dyeing. W. Happe. *Melliand Textilber.*, **34**, 525–527 (June); 650–652 (July); 760–763 (Aug. 1953).

A review of present theories, illustrated with many formulæ, which are very carelessly drawn. Unusual suggestions are—(i) that *o*-nitroaniline will not dye cellulose acetate from tetralin because this solvent, being non-polar, cannot break the internal hydrogen bond of *o*-nitroaniline as does water, and (ii) that the fastness of acid dyes on wool depends on the solubility product of the wool–dye salt. H. E. N.

Theoretical Aspects of the Dyeing Process. H. Wahl. *Bull Inst. Text. France*, (38), 39–60 (April 1953).

Theories providing a basis for the quantitative interpretation of the adsorption isotherms of direct cotton dyes on cellulose are critically discussed. G. L.

General Dyeing Theory. J. Boulton. *Melliand Textilber.*, **34**, 436–438 (May); 527–530 (June 1953).

A review with 40 references. H. E. N.

Hank Dyeing of Rayon. R. Schmidt. *Melliand Textilber.*, **34**, 530–531 (June 1953).

Hints on how to avoid faults in handling the goods from their receipt to their dispatch. H. E. N.

Rayon Crêpes—Dyeing, Printing, and Finishing. K. Bürgers. *Melliand Textilber.*, **34**, 341–343 (April); 449 (May); 542 (June 1953).

A discussion from the practical point of view, including a consideration of the construction of suitable winch machines for dyeing crêpes. H. E. N.

Effect of Metal Salts on Oxidation Colours. A. Ginzel. *Melliand Textilber.*, **34**, 532 (June 1953).

Before dyeing fur with oxidation colours (Ursols), it is usual to treat it with a solution of a metal salt (Cr, Fe, or Cu) for 3–18 hr. at 25–32°c. This speeds up the oxidation and gives colours of greater intensity, covering power, and fastness. If the treatment with metal salts follows dyeing, even better fastness results. H. E. N.

Chemical Modification of Wool to improve the Fastness to Washing of Dyeings. P. Alexander. *Melliand Textilber.*, **34**, 756–757 (Aug.); 855–857 (Sept. 1953).

The carboxy groups of wool can be esterified in alcohol or in aq. soln. using epoxides and related cpd. In the latter class only epichlorhydrin proved effective, crosslinking of the chain-molecules occurring at the same time. In the former, the larger the alcohol the smaller the proportion of carboxy groups esterified. The esterified wool has affinity for equalising acid dyes in a neutral bath and the dyeings show greater fastness to washing than when prepared normally on untreated wool. This conforms to theory. Unfortunately, the ester groups are readily hydrolysed in alkaline media. The process may have significance in dyeing chlorinated wool, regenerated protein fibres, and in the production of two-coloured effects on all-wool fabrics. H. E. N.

Effect of Formaldehyde on Dyed Wool. E. Schempp. *Melliand Textilber.*, **34**, 338–340 (April 1953).

Only 10% of present wadding materials consist of wool or horsehair, the others are made of fibres which have been crease-resisted. During pressing, most of the latter release formaldehyde (I), which often causes a change in shade of the adjacent dyed wool. Previously less serious effects have been traced to I, e.g. from packing paper and boxes. The dyer could help by washing off well, as acid favours reaction with I, and the dyestuff-manufacturer by indicating the fastness of dyes to I. It is remarkable that even some metal-complex dyes are not absolutely fast to I. A simple test consists of sewing together wadding and fabric, covering with a moist piece of cotton, and ironing until dry. H. E. N.

Dyeing of Silk–Polyamide Mixtures. U. Schimmel. *Melliand Textilber.*, **34**, 438–440 (May 1953).

Recipes and tables of the suitability of dyes (FBy and Basf) are given. H. E. N.

Action of Lignosulphonic Acids as Mordants or Carriers of Auxochromic Groups in Additive Dyes. J. B. Puig. *Ion*, **13**, 208–214, 222 (1953): *Chem. Abs.*, **47**, 10854 (25 Oct. 1953).

In dyeing cellulose with additive dyes (i.e. those without affinity for the fibre but requiring additives for fixation) lignosulphonic acids may function in binding the dye to the fibre by means of co-ordination forces between the lignosulphonic acids, the additive (mordant) and the dye. The auxochromic groups in these acids may influence the formation of the final colour of the dyed fibre. C. O. C.

PATENTS

Continuous Chrome Mordanting and Dyeing of Wool. Pacific Mills. *USP* 2,628,883

The cloth is first padded with a hot aqueous solution of a wetting agent and a hexavalent chromium salt, and then alternately and repeatedly passed through a hot acid bath and then through steam so as to reduce the chromium to the tervalent state, then steamed while still wet and acid for an appreciable time and finally neutralised or washed free from acid. The cloth can then be immediately dyed with a mordant dye. Apparatus on which the processing can be carried out continuously is described. C. O. C.

Colouring Polyester Fibres. I.C.I. *BP* 700,171

Treatment with an aqueous dispersion of an unreduced vat dye under superatmospheric pressure and >100°c. gives dyeings of good depth and fastness. C. O. C.

Increasing the Hot-strength and Affinity for Dyes of Polyacrylonitrile Fibres (VI this page).

IX—PRINTING

Glycerol Substitute for Printing. W. Müller. *Melliand Textilber.*, **34**, 766–767 (Aug. 1953).

Sorbitol (Karion F Liquid, E. Merck, Darmstadt), manufactured from grape sugar, is marketed as a substitute for the relatively expensive glycerol in direct printing and vat-discharge pastes. It is at least equally satisfactory. Illustrated by 3 patterns. H. E. N.

Colloresin Process. G. Bernady and W. Küppers. *Melliand Textilber.*, **34**, 443–445 (May); 538–542 (June 1953).

This is a method for the direct printing of vat dyes, carried out in 2 stages and introduced by IG in 1927. The dye is applied alone except for a special thickener, which coagulates on contact with alkalis. The dried prints are padded with an alkaline soln. of a reducing agent and then developed and fixed by steaming, either immediately in the wet state or after intermediate drying. The historical development of the process, the extent to which it has established itself, its advantages and fields of application, and the practical details are described. H. E. N.

Warp Printing. H. Müller. *Melliand Textilber.*, **34**, 441–442 (May 1953).

The development of the only warp printing plant in the world at Textilwerk Münchberg GmbH., Münchberg, Oberfranken, is described. The printed warp gives a material equally patterned on both sides. The definition of the design is less than in normal printing, but a pleasant restful appearance results. H. E. N.

PATENTS

Diazotype Developers containing Fluorescent Brightening Agents. Chemische Fabriek L. van der Grinten. *BP* 700,798

Addition to diazotype developers of a blue-fluorescent salt of a *pp'*-diaminostilbene-*oo'*-disulphonic acid containing a 1:3:5-triazine ring attached to one or both amino groups results in improvement in the appearance of the final prints. C. O. C.

Colour Photography. P. Raiborn. *USP* 2,628,902

Production of several superposed colour images in a single light-sensitive emulsion. C. O. C.

Photographic Multilayer Colour Film and Masking Process thereof. General Aniline. *BP* 701,039

A method of producing integral correction masks during the processing of multilayer colour material. C. O. C.

Colour Photography—Tricolour Separations. General Aniline. *USP* 2,628,901

Solubilising Agents for Leuco Esters of Vat Dyes (III p. 95).
Flock Effects (VI p. 97).
Velvets Electrostatically Produced (Flocking) (VI p. 97).
Bonding Fibres to the Fabric Surface (VI p. 97).
Rayon Crêpes—Dyeing, Printing, and Finishing (VIII p. 98).

X—SIZING AND FINISHING

Sizing of Tinted Viscose Rayon by Linseed Oil Solutions. J. Pinte and M. Essertel. *Bull. Inst. Text. France*, (38), 31–38 (April 1953).

Sighting colours on viscose rayon function as antioxidants retarding the rate of drying of linseed oil and protecting the sized yarn from degradation. The effect is greater when the dye is applied with the linseed oil from soln. in benzene, although it is appreciable on pretinted material. When the benzene soln. contains more than 0·1% dye the sized yarn may remain tacky after drying for 40 hr. at 45°*c*. G. L.

Pathogenic Bacteria and Textiles. M. Nopitsch. *Melliand Textilber.*, **34**, 644–645 (July); 752–753 (Aug.); 852–854 (Sept. 1953).

The carrying of pathogenic and saprophytic bacteria by textiles is of concern in personal hygiene, in the spreading of certain illnesses, and in hospitals. Disinfection of textiles can be carried out by mechanical agitation, washing, exposure to sunlight, heat, steam, and by chemical methods. A method of testing the bactericidal properties of textiles is described. The bactericidal properties of various phenols on textiles were investigated. Chlorocresol and trichlorophenol proved bacteriostatic. Their metal salts were more resistant to washing, but although Cu and Zn salts were very good and Hg salts even better, a wash-fast, colourless, cheap, bactericidal finish has not yet been achieved. As bacteria cause the production of odour from perspiration, the bactericidal cpd. could usefully be applied to dress-shields. H. E. N.

Improvement of Odour of Textiles. K. Bergwein. *Melliand Textilber.*, **34**, 765–766 (Aug. 1953).

Dispersions of perfume-carrying polymers can be applied from the liquor of the final wet treatment. H. E. N.

Microbe-resistant Wool by Chemical Modification—I. H. Zahn and H. Wilhelm. *Melliand Textilber.*, **34**, 609–615 (July 1953).

The resistance of yarn was tested by burial in good garden soil and expressed as the half-life in days (I), i.e. the time during which the breaking strength was halved. The yarn was also examined for alkali solubility (II; N/10 NaOH, 65°c., 1 hr.), acid solubility (III; 4N-HCl, 65°c., 1 hr.), supercontraction (IV; in 50% aq. phenol), and cystine content (V; colorimetrically using phospho-9-tungstic acid). Treatments investigated were: (1) those with monofunctional reagents: (*a*) N/10 HCl in methyl alcohol, room temp., 6 days); (*b*) epichlorhydrin (5% aq. soln. 95°c., 2 hr.); (*c*) acetic anhydride (reflux, 30 min.); (*d*) dinitrofluorobenzene (in aq. alcoholic $NaHCO_3$, 40°c., 14 hr.); (*e*) nitric acid (1% soln., 100°c., 3 hr.). (2) Those involving disulphide bonds: (*a*) reduction (thioglycollic acid in lime water, 50°c., 3 hr.); (*b*) methylation (reduced wool, methyl iodide, $NaHCO_3$ in boiling aq. acetone); (*c*) ethylene-crosslinking (reduced wool, 1:2-dibromoethane, $NaHCO_3$ in boiling aq. acetone, 4 hr.). (3) Those with bifunctional reagents: (*a*) 4:6-bis-chloromethyl-*m*-xylene (in boiling aq., acetone containing $NaHCO_3$, 5 hr.); (*b*) formaldehyde (2% soln. in boiling N/20 H_2SO_4, 2 hr.); (*c*) butanediol bischloromethyl ether (in CCl_4 containing pyridine, 50–55°c., 3 hr.); (*d*) "tetramethylolacetylenediurea" (Kaurit 140, Basf, in aq. ammonium nitrate, room temp., 1 hr.; centrifuged and baked, 130°c., 30 min.). (4) Other: (*a*) KCN (M/10, 66°c., 16·5 hr.); NaOH (N/100, 66°c., 16·5 hr.); (*c*) NaOCl (1 g./l. available chlorine, 15°c., 10 min.); (*d*) alcoholic KOH (2% in 95% alcohol, 22°c., 15 min.); (*e*) dry heat (130°c., 24 hr.); (*f*) 10% Eulan new (0·33% soln. in 0·13% H_2SO_4, 100°c., 1 hr.); (*g*) 2:4:5-trichlorophenol (1% alcoholic soln.); (*h*) 2:4:5:6-tetrachlorophenol (1% alcoholic soln.); (*i*) pentachlorophenol (1% alcoholic soln.). The results obtained are as follows—

Treatment	I	II	III	IV	V
None	14 days	12·0%	14·1%	55·0%	11·5%
1(*a*)	17	15·4	17·1	5·3	—
(*b*)	>25	19·1	32·7	4·6	8·1
(*c*)	>25	70·3	20·8	10·7	10·1
(*d*)	>25	21·7	5·6	10·3	10·8
(*e*)	10	83·3	19·9	17·4	11·7
2(*a*)	6·5	47·6	38·7	—	—
(*b*)	6·5	30·4	90	26·9	7·1
(*c*)	6	5·4	20·2	—	7·3
3(*a*)	58	6·7	16·2	8·6	6·3
(*b*)	21	8·4	8·6	1·6	10·5
(*c*)	25	6·0	9·2	—	10·0
(*d*)	23·5	6·7	10·9	33·2	—
4(*a*)	7·5	10·5	23·4	22·4	4·0
(*b*)	8	4·4	16·9	12·5	5·5
(*c*)	13	22·4	22·9	54·0	11·3
(*d*)	7	13·4	17·3	—	12·7
(*e*)	14	11·8	15·9	35·8	—
(*f*)	25	—	—	—	—
(*g*)	30	—	—	53·8	—
(*h*)	21	—	—	50·6	—
(*i*)	32	—	—	42·9	—

There is no direct connection between microbial attack and alkali or acid solubility. It is not necessary to crosslink wool in order to raise I, but bifunctional reagents lower II at the same time, which is desirable. It appears that a reduction in the capacity to swell is important. Surprisingly, the Harris method (2*c*) is unsuitable. In modified, fresh work, 4(*f*) has given a half-life of 71, 3(*a*) of 105, and 1(*d*) of >115 days. Numerous references. H. E. N.

Protein Modification by Reaction with *N*-Carboxyamino Acid Anhydrides. R. R. Becker and M. A. Stahmann. *J. Biol. Chem.*, **204**, 745–752 (Oct. 1953).

The initiation of the polymerisation of *N*-carboxyamino acid anhydrides by proteins was shown to result in the attachment of unsubstituted amino acids and peptides to proteins. Crystalline bovine plasma albumin and crystalline chymotrypsin were treated with *N*-carboxyglycine anhydride in phosphate-buffered solutions at pH 7·4. Amino acid analysis of the modified proteins by ion exchange chromatography showed an increase of 171 moles of glycine per mole of albumin and of 65 moles per mole of chymotrypsin; the yields were quantitative, based on the protein. Both proteins remained completely soluble, with no evidence of denaturation. The glycine was attached as peptides containing an average of about 7 amino-acid residues. Similar experiments carried out with other *N*-carboxyamino acid anhydrides indicate that the method may be applicable to many *N*-carboxyamino acid anhydrides and to a variety of proteins. P. G. M.

Modification of Viscose and Acetate Rayons by Water Vapour. J. Pinte, M. Pierret, and P. Rachas. *Bull. Inst. Text. France*, (40), 7–42 (June 1953).

The extent of swelling in water, the anisotropy of swelling, the amount of dye adsorbed at equilibrium, and the rate of dissolution in solvents are diminished by steaming, but the degree of polymerisation and the X-ray diagram of the cellulose are not affected. Density, moisture regain, and dye diffusion coefficients are increased. The effects are greater in acetate rayon than in viscose rayon. An attempt is made to explain the experimental data in terms of changes in hydrogen bonding and orientation occurring in the amorphous regions of the fibres. G. L.

PATENTS

Making Cellulose Fibres Resistant to Heat Ageing. United States Rubber Co. *BP* 699,788

The fibres are impregnated with a water-soluble 2:2′-diaminodialkylsulphide. C. O. C.

Dimensional Stabilisation of Fabrics. Bleachers' Association. *BP* 700,413

The selvedges are compressively shrunk and the fabric immediately fed into a tenter where it is stretched widthwise. C. O. C.

Flameproofing. Glenn L. Martin Co. *BP* 700,604

Modification of *BP* 688,372.

The material to be flameproofed is treated with a solution or dispersion of the monomeric or partly polymerised phosphoric acid compounds used as the starting material. When the monomer is used it is partly polymerised on the material which is then dried, passed through a vessel containing the halogen either as a vapour or in solution and finally neutralised with dilute alkali. C. O. C.

Neutralising Composition for use in the Cold Permanent Waving of Hair. Procter & Gamble Co. *BP* 699,997

Addition of a small proportion of an alkali metal salt which in aqueous solution generates H_2O_2, e.g. a perborate, enables the amount of alkali metal bromate needed for neutralising to be greatly reduced. C. O. C.

Increasing the Hot-strength and Affinity for Dyes of Polyacrylonitrile Fibres (VI p. 98).

Rayon Crêpes— Dyeing, Printing, and Finishing (VIII p. 98).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

PATENTS

Mineral-coated Paper. Paper Patents Co. *BP* 700,743

A mineral coated paper for rotogravure printing is made by applying to at least one side of a paper web containing $\leqslant 15\%$ of strong chemical pulp and having a basis weight of 20–100 lb. per ream of 25 × 38 in., 500, a coating including a mineral pigment and an adhesive (a mixture of carbohydrate adhesive material and a synthetic latex), drying the coating to $<10\%$ moisture content, and then super-calendering the paper. The coating is slightly plastic after it has been applied and dried, and very little penetration into the web occurs. The coating contains for each 100 parts by weight of pigment approximately carbohydrate adhesive (3–25 parts), synthetic latex (2–15), latex stabilising agent (0·05–2·0), pigment dispersing agent (0·2–1·0), and fatty acid anti-dusting agent (0·1–1·5), and the total weight of dried coating being 2·5–15 lb. per side per ream. S. V. S.

Felted Vegetable Fibre Web Material. ICI. *BP* 700,805

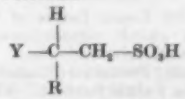
A suspension of vegetable fibre suitable for making paper or paper board is made in water containing a water-soluble salt of a carboxyalkyl cellulose to which is added an aluminium salt and dispersed rosin, and at any stage prior to the felting operation is added a substance yielding amino-polyacetate ions wherein each N atom attached to an acetate radical is a tertiary N atom and the ions being of the kind known to prevent precipitation of aluminium soaps in water and being in an amount sufficient to prevent precipitation of or to redissolve any Al salt of carboxyalkyl cellulose. The ions may be included in the suspension before the addition of an Al salt and may be derived from the mono- or di-Na or the NH_4 salts of nitrilotriacetic or ethylenediaminetetra-acetic acid. S. V. S.

Nitrogen-containing Thermosetting Resins having Aliphatic Sulphate and Sulphonate Residues. Monsanto. *BP* 700,810

A nitrogen-containing thermosetting resin containing residual aliphatic sulphonate or sulphate groups consists of the condensation product of 1 mol. of urea, thiourea, cyanamide, dicyandiamide or guanidine, 2–3 mol. of an aldehyde, e.g. formaldehyde or paraformaldehyde, in alkaline aqueous solution at pH 7·2–8·5 at 50°–70° C., and 0·05 to 0·5 mol. of a water-soluble salt of an amino aliphatic acidic compound of formula NH_2–R–X (R = alkylene of 1–5 C; X = sulphonic or sulphuric acid group). Added to paper stock (0·25–5·0% on the dry wt. of the stock) results in paper made from the stock having high wet strength. S. V. S.

Nitrogen-containing Thermosetting Resins including Organic Sulphonate Residues. Monsanto. *BP* 700,809

A water-soluble nitrogen-containing thermosetting resin containing organic sulphonate residues in the resin molecule and being the condensation product of 1 mol. of urea, thiourea, cyanamide, dicyandiamide, guanidine or aminotriazine, e.g. melamine, 2–6 mol. of an aldehyde, e.g. formaldehyde or paraformaldehyde, and from 0·05 to 0·5 mol. of a water-soluble salt of a hydroxybenzenesulphonic acid which does not contain additional substituents, or a water-soluble salt of an organic hydroxy sulphonic acid of formula—



(R = a phenyl group or an hydroxy alkoxy group of <5 C; Y = H when R = hydroxy alkoxy or OH when R = phenyl). When added to paper stock (0·25–5·0% on the dry wt. of pulp) it results in paper made from the stock having high wet strength. S. V. S.

Rosin Sizes for addition to Paper Pulp. Monsanto Chemical Co. *USP* 2,628,918

A partially or wholly neutralised aqueous dispersion of rosin is added to the pulp using 0·25–4·0% of rosin on the dry weight of the pulp. This is followed by adding a dilute aqueous dispersion containing, on the weight of the rosin first added, 5–40% of the reaction product of rosin with an acidic compound containing the –CO·C:C– group. Finally aluminium sulphate is added to fix the size on the fibres. C. O. C.

Plasticisers for Thermoplastic Polymers (XIII p. 101).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Polypeptide Formation by Reaction of *N*-Carboxy-amino Acid Anhydrides in Buffered Aqueous Solutions. R. R. Becker and M. A. Stahmann. *J. Biol. Chem.*, **204**, 737–744 (Oct. 1953).

The *N*-carboxyanhydrides of glycine, L-leucine, γ-ethyl L-glutamate, and DL-phenylalanine were spontaneously polymerised in aqueous buffered solutions to form polypeptides in high yields under essentially physiological conditions of pH and temperature. The average chain length of the insoluble polypeptides formed varied from 7 for L-leucine to 17 for γ-ethyl L-glutamate. The reaction with *N*-carboxyglycine anhydride proceeded best at pH values near neutrality and in phosphate or citrate buffer. P. G. M.

PATENT

Plastic-coated Leather. R. Hagen. *BP* 699,755

A plasticised thermoplastic coating is bonded to the leather by means of heat and pressure, the leather being simultaneously cooled on the uncoated side. After brief heating of the coated side under pressure the coated leather is allowed to cool before the pressure is removed. C. O. C.

XIII—RUBBER; RESINS; PLASTICS

Resistance of Plastics to Corrosion by Sodium Chlorite Solutions. J. Meybeck and N. Iwanow. *Bull. Inst. Text. France*, (39), 23–37 (May 1953).

Whilst plastics vary in resistance to chlorite soln., they differ from metals by not causing catalytic decomposition.

Polyvinyl chloride and polyethylene are not attacked by chlorite solns., and since they are slightly thermoplastic temps. $<60°$c. must be used. Polytetrafluoroethylene withstands higher temperatures. Urea–formaldehyde plastics, acrylic polymers, and polyamides are slightly affected after prolonged exposure. G. L.

Modification of Phenol–Formaldehyde Resins by 1:2-Epoxides. T. G. Harris, R. H. Horning and H. A. Neville. *Modern Plastics*, **31**, (4), 136, 138, 140, 220, 223 (Dec. 1953).

When phenol-formaldehyde condensates are treated with 1:2-epoxides at various stages of condensation, epoxide addition occurs at the most highly ionised position on the molecule and is catalysed by alkalis through production of phenolate ions. Progressive conversion of phenol groups to ether linkages reduces the thermoplastic properties of the resin until with complete conversion a stable polyhydric alcohol is produced. Esterification of these alcohols with organic acids yields a variety of products ranging in properties from plasticisers to materials which harden by air-drying or heat conversion. C. O. C.

Colour in Plastics. C. Musgrave. *Plastics Inst. Trans.*, **21**, 80–95 (1953).

A review of the general behaviour of the various classes of colouring materials suitable for use with plastics, light fastness, chalking or blooming, and migration or bleeding. The following table broadly summarises the conditions which a colour is required to meet and the main classes of colouring matters used for a particular application—

	Plastic	*Processing Conditions and Properties needed*	*Suitable Colouring Matters*
1	Phenol–formaldehyde mouldings and laminates	Mildly alkaline reducing atmosphere Moulding temperatures up to 170°c. Usually only moderate light fastness	Organic pigments Lakes (toners) Spirit-soluble acid dyes Spirit- and hydrocarbon-soluble dyes Inorganic pigments
2	Phenol–formaldehyde surface coatings and cast resins	Mildly acidic or mildly alkaline reducing atmosphere Long heating at moderate temperature Better light fastness than for moulded products	Organic pigments Lakes Spirit-soluble acid dyes Spirit- and hydrocarbon-soluble dyes Phthalocyanine pigments Inorganic pigments
3	Urea– and melamine–formaldehyde products	Mildly acidic reducing atmosphere for a short period Superlative light fastness	Organic pigments Lakes Fanal pigments Few water-soluble dyes Vat dyes Phthalocyanine pigments
4	Casein	Low mixing and extracting temperatures (ca. 100°c.) Acidic reducing conditions during formulation Moderate–good light fastness Must not bleed into the formulating solution	Organic pigments Lakes Water-soluble acid and direct dyes Phthalocyanine pigments
5	Cellulose plastics (cellulose acetate, cellulose acetate-butyrate, ethyl cellulose, etc.)	Substantially neutral to mildly acidic atmosphere Mixing time of the order of 15 min. at up to 180°c. Short high-temperature injection (180–200°c.) Moderate–good light fastness	Organic pigments (except those prone to chalk) Lakes Basic dyes Spirit- and hydrocarbon-soluble dyes Disperse dyes
6	Polyvinyl chloride and copolymers	Tends to become acidic during processing High temperature compounding (up to 170°c. for long periods) Very good fastness to light High degree of dispersibility	Organic pigments (except those prone to chalk and migrate) Lakes Vat dyes Phthalocyanine pigments Inorganic pigments
7	Polystyrene	Processing conditions neutral but residual oxidising catalyst may be present High temperature processing and injection (200°c. and above) Good to excellent light fastness High degree of dispersibility	Organic pigments Lakes Hydrocarbon-soluble dyes Phthalocyanine pigments Inorganic pigments
8	Polyethylene	Neutral inert processing conditions High temperature processing and extruding, depending upon the grade Very good fastness to light	Organic pigments (except those prone to chalk and migrate) Lakes Vat dyes Phthalocyanine pigments
9	Polymethyl methacrylate	Strongly oxidising atmosphere during polymerisation Moderate temperature Very good fastness to light	Organic pigments Hydrocarbon-soluble dyes Vat dyes Phthalocyanine pigments

C. O. C.

PATENTS

Chemically Resistant Urea–Formaldehyde Resins. Chemische Werke Albert. *BP* 700,708

Incorporation of $>30\%$ of resinous epoxides in urea–formaldehyde resins improves their chemical stability particularly to the action of alkalis and acids. The resinous epoxides are obtained by condensing hydric phenols with epi- or di-chlorohydrin in presence of alkali. C. O. C.

Plasticisers for Thermoplastic Polymers. Petrocarbon. *BP* 700,366

Compounds of formula—

$$C_{10}H_7CH_2(OC_2H_4)_x(OC_3H_6)_yOR$$

(x and $y = 0$ or a whole number; $x + y = 1 - 4$; R = H, or Alk or Acyl of <11 C) are plasticisers for cellulosic or vinyl plastics or the like. C. O. C.

Biphenylyl Esters of Aliphatic Acids as Stabilisers for Polyvinyl Chloride. Dow Chemical Co. *BP* 700,847

The biphenylyl esters of aliphatic acids of 10–18 C stabilise polyvinyl chloride against discoloration on prolonged heating. C. O. C.

Reducing the Tendency of Polymers to accumulate Electrostatic Charges. ICI. *BP* 700,356

The tendency of polymers containing at least one $CH_2{:}CH_2<$ group per molecule to accumulate electrostatic charges is reduced by incorporation of a sulphated long chain alcohol of 10–32 C. C. O. C.

Coated Polystyrene. Nash-Kelvinator Corpn. *USP* 2,628,923

Coatings having good adherence to polystyrene plastics are based on a mixed cellulose ester of hydroxyl content $<1{\cdot}8\%$, e.g. cellulose acetylbutyrate. C. O. C.

Heat Stabilisation of Polyamides. DuP. *USP* 2,630,421

0·1–2·0% of 2-mercaptobenziminazole is used, better results as regards colour stability being obtained if a small amount of a phosphorous acid or its ester or salt is also incorporated. C. O. C.

Heat Stabilisers for Vinyl Resins. S. S. Caldwell, G. J. Chertoff, and G. B. Curtis. *USP* 2,629,700

Certain stannous compounds, particularly stannous salts of fatty acids, are far more effective than the stannic compounds hitherto used for heat stabilising vinyl resins. C. O. C.

Stabilising Vinyl or Vinylidene Chloride-containing Polymers to Heat and Light. Dow Chemical Co. *BP* 701,250

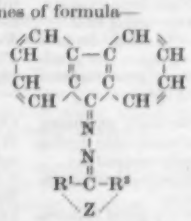
The fully-divided virgin (i.e. unmodified) polymer is wetted with an aqueous solution of an alkali metal pyro- or orthophosphate or phosphite at pH 3·5–5·0 and drying so that 0·05–2·0% by wt. of the phosphate or phosphite is present in the dried product. C. O. C.

Stabilising Vinylidene Chloride—Vinyl Chloride Copolymers. Dow Chemical Co. *BP* 702,633

Copolymers of vinylidene chloride (85–95%) and vinyl chloride (15–5) containing a peroxide catalyst (< 0·1) are stabilised against thermally induced viscosity but not against chemical decomposition by incorporation of pyrocatechol, resorcinol, hydroquinone or *p-tert.* butyl catechol, using at least 0·15–3·0 parts by weight of the dihydrophenol per 1 part of catalyst calculated as benzoyl-peroxide. C. O. C.

Light Stabilisers for Vinylidene Copolymers. Distillers Co. *BP* 701,996

Fluorenone azines of formula—



(R^1 = subst. or unsubst. hydrocarbon radical; R^2 = H or a subst. or unsubst. radical; or R^1 and R^2 together form part of a cyclic radical. Z = nil or atoms to complete a cyclic radical) are used. C. O. C.

Preshrinking Crystalline Vinylidene Chloride Copolymer Film. Dow Chemical Co. *BP* 702,810

The film is rendered dimensionally stable at up to 212°F. by passing it under tension over a series of > 3 rotating smooth cylindrical surfaces separated from one another so that both sides of a given area of film are never in contact with two such surfaces at the same time. At least the intermediate two of these surfaces are at independently controlled temperatures of < 200°F. The total time of contact of the film with these surfaces is 1·5–20·0 sec. C. O. C.

Dialkene Phosphonamides and their Derivatives as Flame- and Waterproofing Agents, Coatings, etc. (III p. 95).

XIV—ANALYSIS; TESTING; APPARATUS

Titanium Dioxide as a Pigment for Coated Papers and its Detection in Paper. K. Berndt. *Das Papier*, **7**, 230–235 (1953); *Chem. Abs.*, **47**, 10848 (25 Oct. 1953).

An account of the production, properties and uses of TiO_2 compared with those of other pigments in paper making. Preliminary tests for TiO_2 in papers can be made by using ultraviolet radiation but these should be confirmed by treatment with conc. H_2SO_4 followed by dilution and addition of 3–6% H_2O_2 which gives yellow to orange red due to TiO_2 hydrate. C. O. C.

Chemical Determination of Amino Groups in Polyamides. H. Zahn and P. Rathgeber. *Melliand Textilber.*, **34**, 749–752 (Aug. 1953).

The method is based on the work of Sanger, *Biochem. J.*, **39**, 507 (1945). Polyamide (1 g.), purified with Leonil soln. (0·5%, 30 min.), washing, drying, and soxhlet extraction (petrol ether, 12 hr.), is treated with a mixture of dinitrofluorobenzene (DNP; 0·5 g.) in alcohol (30 c.c.) and $NaHCO_3$ (0·5 g.) in water (10 c.c.) for 8 hr. It is washed and treated with dil. acetic acid (pH 5), pressed, soxhlet extracted with alcohol for 4 hr., and dried. The DNP-polyamide is dissolved in hot propargyl alcohol (100 c.c.) and filtered cold. The soln. is supersaturated and 0·2–0·5% soln. are preferred if the photometer is sufficiently sensitive. A 1% soln. in a 2 cm. tube gives a density of 0·3–0·6 at 420 mμ. At 40°C., 3 hr. is sufficient for the dinitrophenylation. The reliability of the method was checked by preparing and comparing the molar extinction coefficient of DNP-deriv. of ε-aminocaproic acid, ε-aminocapronitrile, and hexamethylene diamine hydrochloride, and of bis-(DNP-aminohexamethylene)adipic diamide. The coefficient per DNP-residue was constant, also Beer's and Lambert's Law were obeyed. The maximum absorption of DNP-deriv. is <420 mμ. *N*:*N'*-Bis-(DNP)-hexamethylenediamine was also prepared, but has insufficient solubility. Dinitrophenylated poly-ε-aminocaproic acid contained no primary amino groups according to Van Slyke's method and absorbed no HCl at pH 2·4. 7 samples of Perlon were used to compare the new method with titration with HCl, the former giving somewhat lower results. 10 analyses on one sample gave values varying between 26 and 30 millimoles DNP-groups/kg. Perlon. After heating a sample of Perlon 8 hr. at 180°C. only 31·5% amino groups were dinitrophenylated even after reacting for 14 days. The method might therefore be used to test for a previous dry-heat treatment. Dinitrophenylated polyhexamethyleneadipamide is not completely sol. in propargyl alcohol, but addition of a few drops formic acid gives a clear soln. Bis-(6-aminohexyl)adipic diamide gave X-ray reflections corresponding to 3·7 A. (d_{001}) and 4·44 A. (d_{200}), which are remarkably similar to those of nylon. The bis-DNP-deriv. yielded 4·35 A. (d_{001}) and 4·5 A. (d_{100}). H. E. N.

Colour Measurement. K. Agahd. *Melliand Textilber.*, **34**, 532–536 (June 1953).

The apparatus used has a light source consisting of a circular neon daylight tube boosted by three mercury-quartz lamps behind ultraviolet filters. By means of yellow, red, and blue filters of Ostwald colour No. 1, 9, and 17, and a photoelectric cell, the colour of the light reflected from a pattern can be measured and then expressed in terms of black, white, and two of the primary colours. H. E. N.

Description of Surface Colours in Scientific Terms. W. D. Wright. *J. Oil & Col. Chem. Assocn.*, **36**, 537–543 (Oct. 1953).

Four characteristics are required for the scientific description of surface colours—(I) The C.I.E. colour specification, supplemented, as required, by the spectral reflection curve of the surface. There is a brief discussion of the C.I.E. system. (II) The colour appearance expressed in terms of the variables used in some suitable colour atlas such as the Munsell or Ostwald system. Colour atlas specifications are fairly closely related to the visual or psychological attributes of colour and though they are, in the absence of a C.I.E. specification, in the nature of recipes, they are of real significance. The relative merits of different colour atlases depend upon the choice of variables used to define the co-ordinates, and upon practical considerations such as the permanence and reproducibility of the samples themselves. (III) Polar curves of luminance factor and chromaticity, supplemented, if necessary, by polar spectral reflection curves of the surface. An immense amount of data is required for a detailed description of even a single surface, a family of spectral reflection curves recorded for various angles of reflection and viewing, together with a polar curve showing the corresponding variation in luminance factor is necessary. (IV) A record of the surface texture in terms of the detailed pattern of the surface, of local variations of the polar reflection curve from point to point of the surface and of the spread of a ray of light within the surface. Although this complexity may seem, from the commercial point of view, excessive and even unwelcome, the commonly used terms such as "Bloom", "Gloss", "Clean", "Cloudy", and "Skittery" (a list of 36 such terms is given) often lead to difficulties in the precise description of a product. Nimeroff (*J. Amer.*

Optical Soc., **42**, 579 (1952)) has successfully related some of these indefinite descriptions with goniophotometric data. An almost perfect correlation was found between distinctness-of-image gloss and the kurtosis index (peakedness of distribution). In view of the capacity of the eye to perceive, interpret, and integrate a complexity of factors to give a unified concept (no matter how indefinite) such as "satiny", correlation between optical and psychological factors will not be easy. The value of such detailed studies e.g. as an aid to the production of surfaces with special properties, is briefly indicated. J. W. D.

Optical Properties of Paints— Basis of Instrumental Measurements. D. L. Tilleard and T. R. Bullett. *J. Oil & Col. Chem. Assocn.*, **36**, 545–568 (Oct. 1953).

The development, improvement, and application of methods for measuring the basic optical properties of paint films necessitates a knowledge of the physical factors viz. the reflection, absorption, and transmission of light by films (the objective approach), and also of those factors which are involved in the personal appreciation of such properties in practice (the subjective approach). The types of method and instruments at present available for the measurement of gloss, opacity, and colour, the principles on which they are based, and their scope and limitations in use, are discussed. There is considerable scope for the design of instruments of improved sensitivity and particularly photo-electric instruments of much greater simplicity; much has still to be learned about the proper interpretation of colour measurements, and of the best use of instruments already available. J. W. D.

Gloss Measurement— Design of Gloss Meters. V. G. W. Harrison. *J. Oil & Col. Chem. Assocn.*, **36**, 569–588 (Oct. 1953).

Extensive experiments in the visual grading of papers of differing gloss, by numerous observers have shown that (i) individual observers may reproduce their grading of a set of papers quite well, but they may differ sharply from one another; alterations in lighting conditions may bring about a marked change in the rating of certain papers, and this is usually of the same order and in the same sense for all observers. (ii) Gloss is not a simple physical property but an appraisal of a physical situation taken as a whole. The various factors involved are weighted differently by different observers under the same conditions, and by the same observers under different conditions. (iii) Satisfactory agreement amongst verdicts becomes more difficult as the gloss increases, and as colours and surface textures diverge. (iv) No universal gloss scale can be established— only a convention, with which individual disagreements must often occur. A gloss convention which is satisfactory for a wide range of papers (but which may require some modification for other materials) is given by the equation—

$$G = S(0{\cdot}390 + 0{\cdot}325 \tanh 20/L) - 100 \tanh [0{\cdot}1158(P - 1)/100]^3$$

G is the "gloss number", and corresponds to the mean judgment of a larger number of observers who compare the surfaces by diffused light such as that coming through a large window without cross-bars. S is the max. intensity of the scattered light (occurring at an angle near 45°); P is the "peakiness" of the polar curve (defined by max. intensity/intensity 5° nearer the normal), and L is the luminance factor of the surface (i.e. the intensity measured normally to the surface); the "gloss number" is thus the weighted mean of these three factors. The measurements involved, and the correlation of the data with the results of visual gradings, are discussed. Nearly all commercial gloss meters are unsatisfactory when considered in the light of the requirements for a precision instrument; these are— (1) Source of light ca. C.I.E. Source "A"; (2) Mean angle of incidence = 45°; (3) Illuminated part of specimen to be a rectangle with the longer side perpendicular to the plane of incidence; (4) Shorter side of above rectangle should not subtend an angle $> 0° 40'$ (3°) at the centre of the collecting lens of the receptor system— the length of the longer side is less important and may be 10 times the shorter side; (5) Incident beam should be in the form of a truncated wedge of vertical angle $\geqslant 0° 30'$ (2° 30'); (6) Beam admitted by the receptor system should be in the form of a similar truncated wedge of vertical angle $\geqslant 0° 30'$ (2° 30'); (7) It must be possible to measure intensities at 0° and also over the range 38–47°. Angle made by the moving arm should be recorded to 0° 5'. (Arm set at fixed angles of 0° and 45°); (8) Spectral sensitivity of the receptor should approximate to the C.I.E. photoptic spectral visual sensitivity function. (Not essential). The bracketed data in the above list represent the deviations and tolerances permissible in a gloss meter for routine purposes. Even the precision instrument cannot deal satisfactorily with matt distempers which exhibit a distinct sheen when viewed from almost grazing angles, or with highly glazed surfaces such as polished metals, gloss paints etc. Ten pages are devoted to the discussion which followed the presentation of this paper. J. W. D.

A Systematic Method for Separating and Identifying Synthetic Colours used in Foods. R. Fouasin. *Rev. Fermentations et Inds. aliment.*, **7**, 195–219 (1953): *Chem. Abs.*, **47**, 12,668 (25 Nov. 1953).

Study of the chromatographic properties of more than 80 food colours has led to the development of a scheme of qualitative analyses for them. The dyes are first separated into groups by nonmiscible solvents, which are then subdivided by various acid or alkaline elements. C. O. C.

Coal-tar Colours. XIV— D&C Red No. 39. L. S. Harrow, K. S. Heine, and W. J. Sheppard. *J. Assoc. Offic. Agr. Chemists*, **36**, 548–553: *Chem. Abs.*, **47**, 12,668 (25 Nov. 1953).

The $TiCl_3$ titration (*A.O.A.C., Methods of Analysis* 7th ed. 1950, Sec. 34–21) and a spectrophotometric method were satisfactory for the quantitative determination of a purified sample of D&C Red No. 39. Spectrophotometric data for aqueous solutions of this dye are given. A spectrophotometric method for the simultaneous determination of uncombined anthranilic acid and *NN*-bis(2-hydroxyethyl)aniline is also described. C. O. C.

Chromatography and Synthesis of Polymethinic Dyes. J. Nys. *Medel. Vlaam. Chem. Ver.*, **15**, 72–89 (1953): *Chem. Abs.*, **47**, 11,737 (10 Nov. 1953).

Chromatographic techniques for purifying azo- and polymethinic dyes are discussed. A new automatic warning apparatus which prevents the columns becoming dry during routine work is described. Examples given of chemical separation and disintegration induced by the adsorbents in the dye molecule. A new synthesis of polymethinic dyes is described. The catalytic influence of alumina, owing to its alkalinity and stabilising influence on the intermediary reaction products, is stressed, because it enables the new synthesis to take place at room temperature and gives pure and high yields. Examples given are the monomethincyanine, carbocyanine and merocyanine syntheses. C. O. C.

Microchemical Reactions in the Analysis of Inks. J. C. B. Graf. *Publs. Inst. Invest. microquím., Univ. nacl. litoral* (Rosario, Arg.), **14**, 95–103 (1950): *Chem. Abs.*, **47**, 12,831 (25 Nov. 1953).

Martini's spartein thiocyanate reagent containing NH_4 thiocyanate (40 g.) and spartein sulphate (5 g.) in water (100 ml.) has been used for detecting Fe in ink. One drop of sample on a microscope slide was treated with a drop of 20% H_2O_2, followed by a drop of spartein thiocyanate reagent. Presence of ferric iron caused a red ppt. containing crystals in the form of prisms and rosettes. The reaction will detect 0·01 *v* but comparison of the microcrystals has not yet been established. Co, V, and Zn cause a similar reaction but the ppt. is not red. Many other Fe tests can be applied to inks. The following was found to be suitable for use on dried writing. Quickly extract a section of the writing with a small drop of 1 : 3 HCl applied by a fine glass needle. Transfer the extract to a slide and add 1 drop of a 1 : 1000 soln. of K acridinethiocyanate. Presence of Fe results in formation of typical crystals. A blank must first be run on the paper itself. C. O. C.

Fluidity of Cellulose containing combined Formaldehyde. V. B. Chipalkatti and N. F. Desai. *J. Sci. Ind. Research* (India), **12B**, 70–2 (1953): *Chem. Abs.*, **47**, 12,801 (25 Nov. 1953).

Cellulose containing combined HCHO is insoluble in cuprammonium solution. H_3PO_4 is suggested as a solvent

and the fluidity values obtained in H_3PO_4 are correlated with values in cuprammonium solution. C. O. C.

Micro-organic Attack on Textiles and Leather. M. Nopitsch. *Ciba Review*, **9**, 3582–3614 (Oct. 1953).

A survey of the whole field is divided into the following sections: The Discovery of the Microbes, Microbial Deterioration of Wool and other Animal Fibres, Microbial Damage to Vegetable Fibres, Decay of Fishing Nets through Microbial Action, Micro-organic Attack on Leather, Identification of Microbial Damage and Culture Methods, Preventive Treatments for Textiles and Leather, and Bibliography. C. O. C.

Silicones — Investigation of Possible Uses (III p. 94).

XV— MISCELLANEOUS

Methyl Octylbenzenesulphonate as a Cause of Dermatitis. C. N. D. Cruickshank and H. Howard-Swaffield. *Brit. J. Ind. Med.*, **10**, 121–124 (1953): *Chem. Abs.*, **47**, 10768 (25 Oct. 1953).

An outbreak of dermatitis in a pilot-plant production of an antistatic lubricant was found to be caused by one of the intermediates, methyl octylbenzenesulphonate, all the persons exposed to it being affected. In the large-scale plant, in which all processes were enclosed, no further dermatitis occurred. C. O. C.

Training of Textile Chemists. H. Rath. *Melliand Textilber.*, **34**, 551–552 (June 1953).

Problems of Recruitment in Textile Finishing. W. Stockhausen. *Melliand Textilber.*, **34**, 553–554 (June 1953).

Fixation of Dyes by Montmorillonite. F. Kayser and J. M. Bloch. *Chimie et Industrie*, **69**, 1054–8 (1953): *Chem. Abs.*, **47**, 12,819 (25 Nov. 1953).

Samples of both H and Na forms of montmorillonite were dried at 105°c., ground, sifted and made into 5% aqueous suspensions. These were treated with 1% aqueous solutions of azo, thiazo, oxazo, diazo, phthalein, acridine, indigo and triphenylmethane dyes. Cationic dyes are strongly and irreversibly adsorbed; electronegative groups in the molecule cause fixation to be weak and elution easy. The more electropositive the dye molecule the less strongly it is held by either form of montmorillonite. Azo dyes are intermediate cases, the electropositive nature of the N groups dominating the negativity of the SO_3H and OH groups, causing some dye adsorption, but with relatively easy elution. Rhodamines are strongly and irreversibly adsorbed in spite of the presence of the free COOH group in Rhodamine B, S and H, and the ester group in Rhodamine 2G and 6G. Dyes lose their visible fluorescence when adsorbed on either type of montmorillonite but adsorbed Rhodamines show blue-violet fluorescence under ultra-violet radiation. The desorption of Neutral Red from H montmorillonite is slight, even with conc. soln. of voluminous cations or by prolonged grinding of the Neutral Red—montmorillonite complex. Mg acetate does not liberate H^+ or Na^+ from a montmorillonite fixed with Neutral Red and the amount of dye fixed is greater than the exchange capacity of the montmorillonite. Adsorption on Na montmorillonite is usually accompanied by colour change, the dye assuming the colour it has in strongly acid media because of the acidic properties in the vicinity of the montmorillonite particles. The mechanism of dye adsorption on montmorillonite is more than simple base exchange even though cationic dyes are strongly adsorbed. The dye displaces H^+ or Na^+ and is then subjected to some further adsorbing action by the montmorillonite. C. O. C.

Protection of Cardiac Glycosides from Action of Light by Actinic Desensitiser (Red Dye). T. M. Feinblatt and E. A. Ferguson. *New Engl. J. Med.*, **246**, 905–6 (1952): *Chem. Abs.*, **47**, 12,751 (25 Nov. 1953).

Removal of the green colour by charcoal followed by adding 0·1% of Amaranth Red or Phenosafranine doubled the shelf life of tincture of digitalis. C. O. C.

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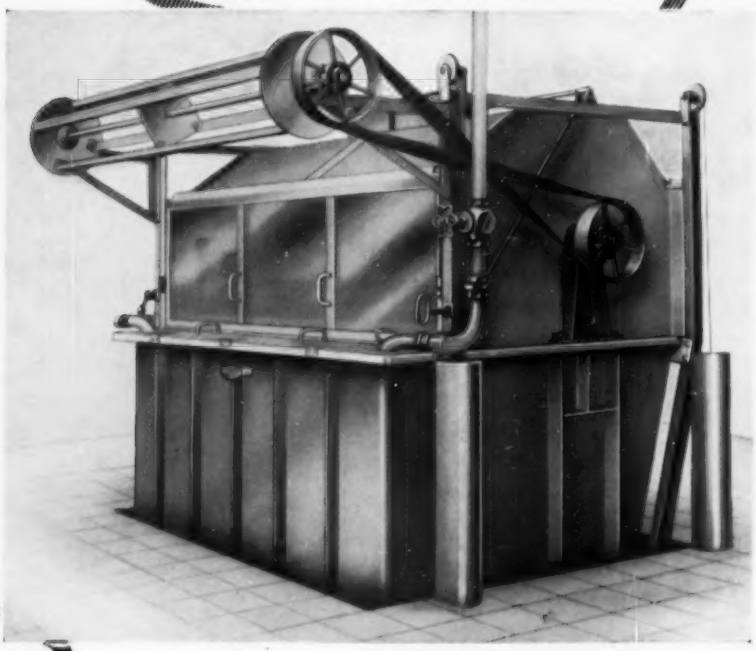

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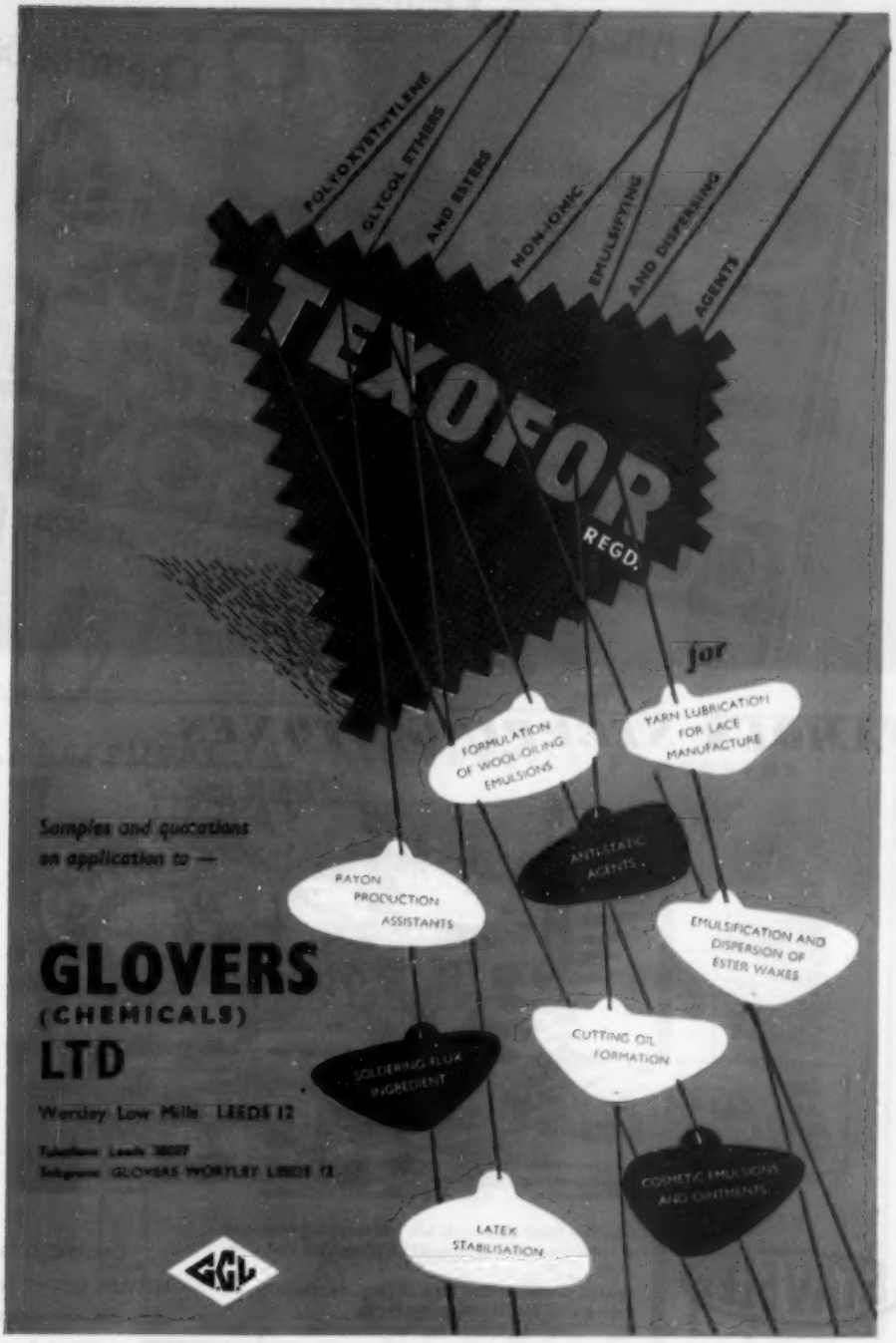
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